THE BEHAVIOUR OF SOLUBLE PETROLEUM PRODUCT DERIVED HYDROCARBONS IN GROUNDWATER

PHASE II

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EXECUTIVE SUMMARY

Introduction

The specific objectives of this three-phase research program are: 1) to critically evaluate small-scale methods for measuring the retardation via sorption of the aromatic hydrocarbons benzene, toluene and xylenes (BTX) as they move in groundwater, 2) to determine the effects of both retardation by sorption and biodegradation on the migration of BTX in groundwaters, and 3) to assess the potential for biochemical remediation or clean-up of groundwaters contaminated by BTX. This report describes the major aspects of progress made in the second phase of this program during 1985.

The Phase I Report (PACE Report 85-3) described the progress from April to December 1984. It described the design, and implementation and initial results of a field experiment where BTX dissolved in groundwater was injected below the water table into a shallow sand aquifer and the migration of BTX monitored as it moved under natural hydrologic gradients through a dense network of monitoring piezometers or wells. The BTX components migrated slower than the groundwater flow rate, (i.e. were retarded) due to sorption by solid aquifer organic material, and the amount of BTX decreased over time, due to biodegradation. Calculations, laboratory tests and a small-scale in situ field test were conducted to predict the retardation by sorption and were found to be in good agreement with the observations from the field experiment.

The specific objectives of the Phase II research are:

1. to complete the field-scale experiment, in order to assess the controls of BTX migration at the field site

2. to critically evaluate laboratory tests, calculations and small-scale field tests designed to estimate sorptive retardation by employing additional sandy materials of higher organic carbon content than the Borden sand (0.02% organic carbon by weight)

3. to evaluate various nutrient addition methods aimed at enhancing BTX biodegradation in shallow sand aquifers.

This report emphasizes the results of the field-scale experiment and of the laboratory tests of sorptive retardation and biodegradation associated with the Borden field site. Future reports will present the evaluation of various methods for estimating sorptive retardation, since the research, begun in Phase II, is continuing into Phase III. Initial laboratory experiments in Phase II suggested that the slow, natural biodegradation of BTX under anaerobic (oxygen-free) conditions is accelerated by addition of nitrate. These tests are continuing into Phase III and field testing of this remedial scheme is also planned for Phase III and so this research will also be presented in future reports.

The Natural-Gradient Experiment and Related Laboratory Tests

Dissolved benzene, toluene, and ortho, meta and para xylene and chloride, injected into a shallow sand aquifer, migrated under a natural flow condition. Intensive three-dimensional sampling established the spatial distributions of the solutes at discreet times during transport. Relative velocities of the organic solutes to that of chloride and the groundwater itself range from 90% for benzene to 65% for m-xylene. Retardation follows the same order and magnitude as that obtained by laboratory batch and column tests, small scale field tests, and predictions based upon the chemistry of the organic solutes. Evidence of irreversible sorptive retardation was not found in the field or laboratory studies.

More than 98% of the mass of each dissolved hydrocarbon was removed by 410 days after injection. The mass losses are initially linear over time followed by a period of tailing or rate reduction. Laboratory biotransformation studies yield similar mass loss rates. Biotransformation products, including phenol, two methyl phenols, two dimethyl phenols, and o-toluic acid have been identified in laboratory studies but no products have been found at the field site.

The injection solution contained only about 0.5 mg/L dissolved oxygen and shallow aquifer had spatially variable, dissolved oxygen concentrations from near zero to about 7 mg/L. When oxygen is present, either initially or through natural transport processes, BTX is removed to levels below detection (1-2 ppb) within a few weeks to a few months. When oxygen is not available or is transported to the BTX slowly, longer persistence (greater than 410 days) is observed. Aquifer heterogeneities in soil structure and dissolved oxygen distribution, in conjunction with sorption and biotransformation, produce surprisingly heterogeneous solute distributions. Hydrocarbons persist longest in specific oxygen-free aquifer layers.

The major conclusion of Phase II studies is that, in low-organic-carbon sand aquifers, the major attenuation process is biotransformation. Oxygen is required, and the major control over the biodegradation rate is the rate of transport or mixing of oxygenated groundwater with the contaminants. This mixing rate is site specific and warrants definition in specific cases of groundwater contamination.

Phase III Projects

In Phase II, laboratory studies of sorptive retardation of BTX in two additional sandy materials, containing 0.06% and 0.1% by weight organic carbon, indicated greater retardation and a greater spread in retardation-values among the organics in each soil. With this greater variation in retardation, it appears possible to test the various measurement procedures, to indicate their relative merits and to recommend a particular procedure as being adequate and/or preferable. This is one of the objectives of Phase III studies.

An additional sampling of the field site is planned to evaluate the possible persistence of benzene at concentration levels of 0.5 to 1.0 ppb. A modification of the current analytical technique will be made to lower the current detection limits for benzene of about 2 ppb. The results will help evaluate the biodegradation process, by establishing whether biodegradation only occurs at benzene concentrations in excess of a few ppb.

The major objective for Phase III is to conduct another field experiment to evaluate: 1) the migration and attenuation of BTX when the complex spectrum of other water-soluble gasoline components is present, and 2) the possibility of enhancing natural biodegradation through the addition of nitrate to contaminated groundwaters. Additional laboratory evaluation of BTX biodegradation in the presence of these other, gasoline-derived organics will augment this field experiment, and the interpretation of the results will be facilitated by the use of appropriate mathematical models currently being developed.

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Chapter I

INTRODUCTION

1.1 Goals and Objectives

The goal of this three-phase research program, initiated in 1984, is to develop an improved understanding of the processes controlling the migration or transport in groundwater, of selected organic compounds that dissolve in groundwater from petroleum products. The specific objectives of this program are five-fold:

1. To assess the accuracy and applicability of the conventional methods and two newly-developed methods for determining the retardation by sorption onto aquifer materials of the selected organic compounds during transport by groundwater in sand aquifers.

2. To develop and assess *practical methods* for determining the extent to which biodegradation will remove the selected organic compounds during migration in sand aquifers.

3. To test and evaluate the balanced nutrient method of stimulating biodegradation as a remedial action for groundwater zones contaminated with the selected organic compounds and to evaluate the role of dispersion in this method.

4. To make use of the information obtained in the three objectives mentioned above in evaluating other options for remedial action that have been described in the literature or are currently being developed.

5. To broaden the results of this study to consider migration and possible remedial actions pertinent to other hydrogeological environments.

This research will aid the petroleum industry and its consultants in the design and use of groundwater monitoring networks, in the assessment of both the rate of migration and the fate of dissolved organic components and in the evaluation of options for remedial measures required to limit or reduce the extent of such contaminants. Specific benefits will include:

1. evaluation of the natural processes that control contaminant movement

2. evaluation of means to assess sorption and biodegradation processes that could slow down and limit the movement of contaminants

3. provision of a scientifically-evaluated in situ tester for field measurement of sorption

4. evaluation of in situ remedial techniques using microbial degradation

5. identification of parameters critical to properly deal with groundwater contamination by BTX (benzene, toluene, xylenes).

Specific tasks undertaken in the initial phase were:

1. the performance of calculations, laboratory experiments and field experiments with an in situ tester to define the sorptive characteristics of the Borden sand for BTX

2. the design and implementation of a natural gradient injection test at the Borden site to evaluate the rate of movement and the fate of BTX dissolved in groundwater. The results are also used to assess the suitability of laboratory tests as predictive tools

3. the critical comparison of the various laboratory and field methods for assessing the slowing down or retardation of BTX in groundwater.

In Phase II, some of these tasks continued and additional tasks were undertaken. The specific Phase II tasks were:

1. to complete the natural gradient injection experiment at the Borden site in order to evaluate the migration of BTX through the aquifer and to compare laboratory estimates of sorptive retardation and biodegradation rates with the observations from the field experiment

2. to assess the ability of the microbial population at the field site to degrade BTX under various environmental conditions and at various initial concentrations and to determine the most significant degradation pathways and degradation products

3. to assess various nutrient additions designed to enhance biodegradation

4. to obtain a more substantial basis for identifying the advantages and limitations of the various procedures to determine sorptive retardation of BTX. This involves comparing the results of calculations and laboratory tests for BTX sorption using additional sandy materials having a range in organic carbon content in order to recommend procedures for a variety of hydrogeologic regimes.

This research commenced in April, 1984 and the progress in Phase I until the end of 1984 is summarized in PACE Report No. 85-3 (Patrick et al., 1985). The Phase I report presented the laboratory and field study of the sorptive characteristics of the Borden sand with respect to BTX as well as the design and initial results of the natural gradient injection experiment conducted within the Borden sand. This Phase II report emphasizes the results of this natural gradient injection experiment and the related laboratory tests of retardation and biodegradation. Other aspects of Phase II research - the expanded sorption testing utilizing additional sandy materials and the microbial testing of potential remedial measures employing enhanced biodegradation methods will be presented in future reports.

1.2 Background and Approach for the Natural Gradient Experiment

The contamination of groundwater by soluble petroleum hydrocarbons is a problem of serious and ongoing concern. Accidental losses of petroleum products to the soil usually invoke alarm because of both the threat posed by gasoline vapours entering buildings and the longer term threat caused by the transport of hydrocarbons, either as a non-aqueous phase or as dissolved components, through an aquifer to supply wells. Several cases of petroleum and petroleum product spills have been documented (eg. NWWA, 1984; PACE, 1983; API, 1983,) although relatively few have directly addressed the issue of dissolved hydrocarbon contamination of groundwater supplies. From the results of laboratory and theoretical investigations (eg. Schwille, 1981, 1975, 1967; Vanlooke et al., 1975; van der Waarden et al., 1971) and limited field information (eg. NWWA, 1984; Yazicigil and Sendlein, 1981; Zoetman et al., 1981) it is possible to make some general observations regarding dissolved hydrocarbon transport in groundwater:

1. The most abundant of the dissolved constituents arising from a mixed hydrocarbon source (eg. gasoline) tend to be the most water soluble, major components in the source.

2. These constituents also tend to travel the furthest within the groundwater system.

3. These constituents can persist for years, particularly when the aquifer is depleted of dissolved oxygen.

Unfortunately, the most soluble hydrocarbon components are also among those of greatest concern as contaminants in both surface and groundwater supplies. Gasolines and similar petroleum products typically contain fifteen percent or more by volume of mono-aromatic hydrocarbons (United Technology and Science, Inc., 1978) which, comparatively, are very water soluble (Table 1.1), impart odours and tastes to water at concentrations of only a few micrograms per litre, and include carcinogenic components. Benzene, is of particular concern because it is both a known human carcinogen (CEQ) and is the most water soluble (approximately 1800 mg/L) member of the group.

Collectively, the mono-aromatic hydrocarbons are commonly referred to as BTX because of the components benzene, toluene (methyl benzene), and the three xylene isomers, ortho-, meta-, and para- (1,2-dimethyl benzene, 1,3-dimethyl benzene, and 1,4-dimethyl benzene, respectively) which are frequently found together in groundwater at petroleum product contamination sites. Many of the compounds have also been individually identified in groundwaters associated with municipal landfills (Barker et al., 1986) and hazardous waste sites (Jackson et al., 1985).

The mobility and persistence of compounds such as BTX in groundwater is a consequence of a number of processes which effect the migration and attenuation of groundwater solutes, including advection, dispersion, sorption, and chemical and biochemical transformations. In many previous field studies it has not been possible to adequately quantify these processes because the initial mass or volume of the solute was unknown or poorly defined, the hydrogeologic regime was not adequately characterized, or the spatial concentration distribution was not sufficiently detailed.

Table 1.1: Chemical Parameters for the Organic Solutes at 25°C.

Solute	Octanol-Water Partition Coefficient	Solubility (mg/L)
Benzene	135 (1)	1791 ± 10 (3)
Toluene	380 (2)	534.8 ± 4.9 (4)
o-Xylene	880 (2)	167.0 ± 4.0 (5)
p-Xylene	1410 (2)	157.0 ± 1.0 (5)
m-Xylene	1580 (2)	134.0 ± 2.0 (5)

(1) Chiou et.al., 1983.
(2) Hansch and Leo, 1979
(3) May, 1980
(4) Sutton and Calder, 1975
(5) Price, 1976.

Recently, however, controlled field studies using inorganic and organic solutes have been conducted under conditions of a natural gradient to assess these processes (Sudicky et al., 1983; Sutton and Barker, 1985; Mackay et al., 1985a, 1985b). In these studies, detailed two- or three-dimensional monitoring networks were used to characterize solute concentration distributions at various discrete times during transport. It was then possible to compare the field observations with the predicted effects of processes independently described by either field or laboratory measurements.

In the present study a similar approach was used to examine those processes which effect the persistence and fate of dissolved monoaromatic hydrocarbons in a shallow sand aquifer (Patrick et al., 1985). A slug of selected constituents was injected as a uniform pulse below the water table and allowed to migrate under a natural gradient through a relatively dense three-dimensional monitoring network. A portion of the network showing the injection site is presented in Figure 1.1. The total network sampled in this study is shown in Figure 1.2. The network, which had for the most part been installed for a previous injection experiment (Mackay et al., 1985), was intensively sampled using specialized procedures at six relatively brief time periods. Data sets have been produced which provide three-dimensional 'snapshots' of each migrating solute. The solute velocities and changes in the size, shape, and total mass of each solute are then evaluated and compared with laboratory and theoretical predictions.

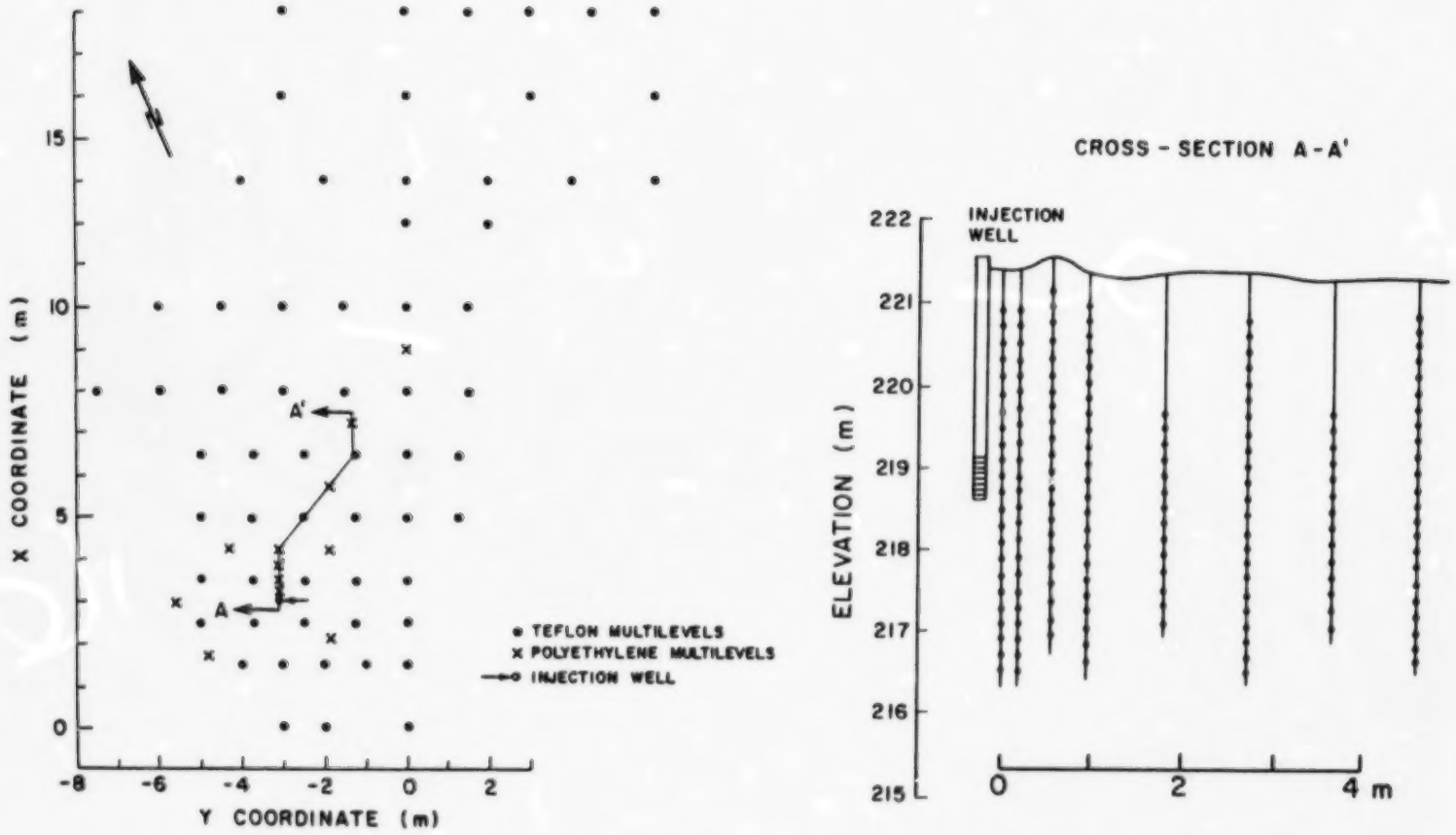
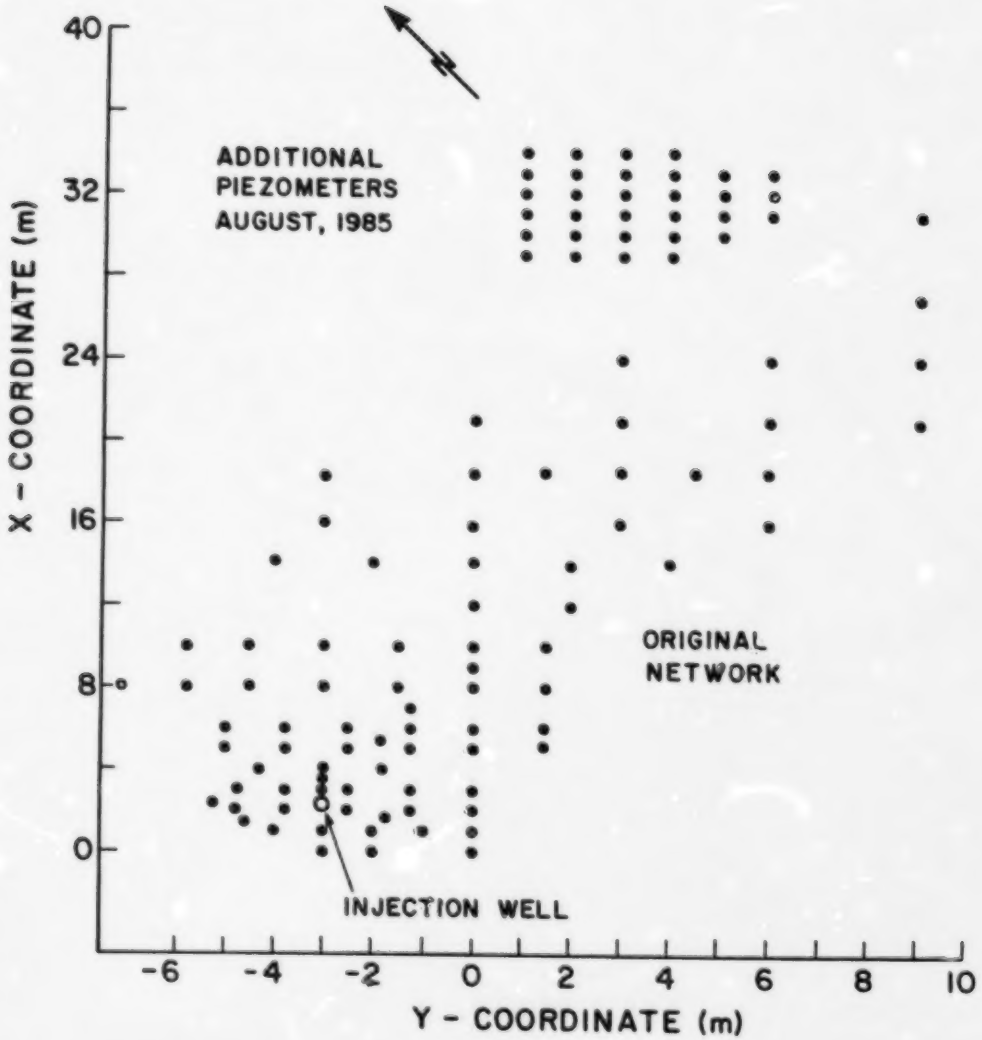


Figure 1.1: Site plan and cross-section showing injection well and multilevel piezometer locations

Figure 1.2: Site plan showing all piezometer locations sampled in this study



1.3 Supporting Laboratory Studies

The field injection experiment defines the migration rate and the persistence of BTX where the controlling processes act in concert. In order to attribute BTX behaviour to the appropriate process, additional laboratory experiments were undertaken to evaluate the retardation of BTX by sorption by Borden sand and to evaluate the rate, controlling factors and products of biotransformation or biodegradation. This report discusses such experiments as they relate to the field injection experiment. Future reports will emphasize both the ongoing evaluation of various sorption tests conducted with additional sands and the ongoing detailed laboratory studies of BTX biotransformation under various environmental conditions.

Chapter II

THE BORDEN TRACER SITE

The experimental tracer site is located in an unconfined sand aquifer underlying an inactive sand quarry at Canadian Forces Base Borden in southern Ontario, Canada. The site was used for a recent large-scale tracer study of inorganic and halogenated organic compounds (Mackay et al. 1985a), and is near two other tracer sites described by Sutton and Barker (1985) and Sudicky et al. (1983). The current test occurred in a part of the site not occupied by the previous injection solution and so has not been effected by the previous experiments.

Major hydrogeologic properties of the aquifer are presented in Table 2.1. At the site, the aquifer consists of fine to medium grained sand of glacio-fluvial origin which extends from the surface to a depth of about 9 m. The sand overlies a relatively thick and impervious silty, pebbly clay. As indicated in Table 2.1, the organic carbon content, the clay size fraction, the specific surface area, and the cation exchange capacity of the aquifer material are all low. The water table is shallow, at a depth of only 0.5 m to 1.0 m. The hydraulic gradient is generally to the northeast, although there is some seasonal oscillation. The lower 3 m to 4 m of the aquifer is occupied by a leachate plume emanating from a nearby abandoned landfill (MacFarlane et al. 1983) while the upper 5 m is unaffected. The sand exhibits significant small scale spatially heterogeneous structures consisting of thin and nearly horizontal lenses of both fine and coarse grained sand. The effective size of the lenses is on the order of 0.1 m thick by 1.5 m long (Sudicky, 1985). Hydraulic conductivity contrasts among layers can be an order of magnitude or greater.

The quality of groundwater from the lower zone occupied by the leachate and from the upper unaffected zone is presented in Table 2.2. Groundwater from the lower zone was used as injection water for the study. Samples of this water were obtained from a well located approximately 70 m to the north of the injection site, while samples from the upper zone were obtained in the vicinity of the landfill (Nicholson et al., 1983) and at the tracer site. Neither the upper or lower zones contain detectable concentrations of BTX. Dissolved oxygen concentrations through section A-A of Figure 1.1 is shown in Figure 2.1. The upper zone contains a approximately 2.0 to 8.5 mg/L dissolved oxygen, while the lower zone is anoxic. A distinct band of low dissolved oxygen (hatched in Figure 2.1) is present in the upper zone at a depth of about 2.5 m.

The upper zone of the tracer site is monitored with a dense three-dimensional array of multilevel sampling piezometers. The main network and the injection site are presented in plan view in Figure 1.1 and the overall network, including additional piezometers installed in August, 1985, in Figure 1.2. The vertical distribution of sampling points along section A-A' of Figure 1.1 is shown in Figure 1.2. The multilevel piezometer design is described by Mackay (1985a) and is pat-

Table 2.1: Hydrogeologic properties of the Borden aquifer (Mackay et al., 1985a)

	Range	Estimated Mean
Hydraulic gradient	0.0035 - 0.0054	0.0045
Hydraulic conductivity	10^{-4} - 10^{-5} m/s	10^{-4} m/s
Porosity	0.38	0.38
Mean Velocity	0.5 - 0.10 m/d N40°E - N53°E	0.09 m/d N47°E
Organic carbon content	0.01 - 0.09%	0.02%
Clay size fraction	0 - 15%	0%
Specific surface area	0.6 - 1.6 m^2/g	0.8 m^2/g
Cation exchange capacity	0.52 meg/100g	0.52 meg/100g
Bulk density	1.68 g/cm^3	1.68 g/cm^3

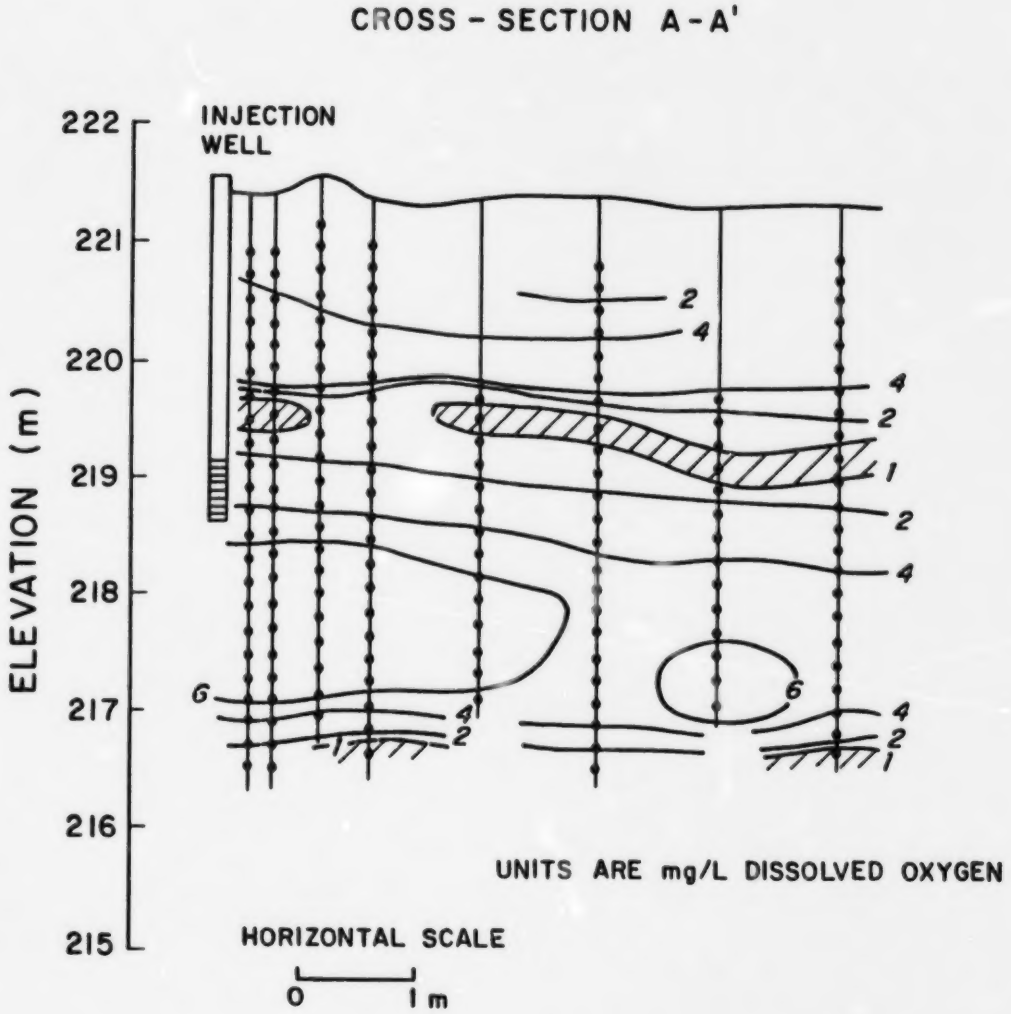
Mackay et al. (1985 a)

Table 2.2: Chemical Characteristics of the Groundwater and Injection Water

Parameter		Upper Zone Groundwater[1]	Low Zone Groundwater-Injection Water[2]
Ca^{2+}	mg/L	50-110	112
Mg^{2+}	mg/L	62.4-6.1	8.0
Na^{+}	mg/L	0.9-2.0	21.5
K^{+}	mg/L	0.1-1.2	0.7
Alkalinity as $CaCO_3$	mg/L	100-250	195
Cl^{-}	mg/L	1-2.8	24.8
NO_3^{-}	mg/L	\0.6	\0.05
SO_4^{2-}	mg/L	10-30	134
TDS	mg/L	380-500	n.d.
DOC	mg/L	\0.7	1.0-2.0[3]
DO	mg/L	0-8.5	0.5-1.5
Temperature	^{o}C	6-12	8-14
pH	---	7.3-7.9	7.4

(1) Mackay et al., 1985 a
(2) This study
(3) Estimated from Nicholson et al., 1983, Figure 2
n.d. not done

Figure 2.1: The distribution of dissolved oxygen through section A-A' of Figure 1.1, prior to injection



terned after a design first described by Cherry et al., (1983). Each consists of a series of 3.2 mm (1/8 inch) outside diameter flexible plastic tubes affixed to a rigid 13 mm (1/2 inch) outside diameter rigid PVC centrestalk. The tube ends are screened and are vertically separated at 0.2 m or 0.3 m intervals. Both the vertical and horizontal separation of the sampling points are compatible with the scale of the structural bedding of the aquifer sand. For the present study, several additional multilevel piezometers were installed in the vicinity of the injection site and in the down-gradient direction to improve the density of the sampling network. These piezometers were constructed with polyethylene tubing, while the original piezometers and those installed further down-gradient in August, 1985 were constructed with teflon tubing.

Chapter III

EXPERIMENTAL PROCEDURES, DATA MANAGEMENT AND ANALYSIS

The selection of the size and composition of the injection solution, the design of an appropriate injection system, and the development of efficient sampling and laboratory analytical procedures benefitted from the experimental design and procedures described by Mackay (1985a) for a previous injection. Details of the design and implementation of the field and laboratory procedure of the present study are described by Patrick et al. (1985), and are summarized herein.

3.1 The Field Injection

The injection system introduced a known volume and concentration of dissolved constituents (Table 3.1) into the aquifer below the water table to form a plume of relatively uniform size and shape while minimizing the disturbance to the natural groundwater flow regime. The solutes for the injection experiment were benzene, toluene, the three xylene isomers, and chloride.

These specific mono-aromatics were introduced, rather than a complex mixture of water-soluble organics which could have been obtained by saturating water with gasoline, because of the requirements for precise, rapid, and inexpensive gas chromatographic analyses. Initial tests indicated that the complex mixture present in gasoline-saturated water would preclude specific mono-aromatic quantitation in view of such analytical requirements. Recent advances, however, make such analyses possible for Phase III studies. The organic solutes, as previously discussed, have been found to persist in many groundwater environments but are sufficiently different chemically that significant differences in sorption effects and biological transformation rates could be expected. Chloride was included in the design solution as a non-reactive and conservative tracer. All available evidence indicates that it behaves conservatively and is non-reactive in the Borden aquifer (Freyberg, 1985; Sudicky et al. 1983) The concentrations of the constituents in the injection solution (Table 3.1) were chosen to approximate those that might be encountered in a realistic contamination setting and that could be easily produced and accurately monitored over the course of the study.

Injection water was obtained from a well located approximately 70 m north of the site that had been screened within the lower landfill leachate zone. Although this water contained significantly higher chloride than water from the upper zone (Table 2.2) it was preferred because it had a negligible dissolved oxygen concentration. Low dissolved oxygen is more characteristic of actual hydrocarbon contamination situations.

Table 3.1: **Estimated Amounts of Chemicals Injected**

Chemical	Estimated Mass	Average Injection Concentration
Benzene	4.25 g*	2360 ug/L
Toluene	3.16 g	1750 ug/L
o-Xylene	231 g	1280 ug/L
p-Xylene	1.94 g	1080 ug/L
m-Xylene	1.96 g	1090 ug/L
Chloride	2.30 kg as Cl^-	1280 mg/L

* actual benzene values may be slightly lower due to contamination by hypovial septa. (Patrick, 1986)

The injection began on 9th August, 1984 and continued for 21 hours at a flow rate of 1.4 litres per minute, introducing 1.8 m^3 of solution to the aquifer. The solution was frequently sampled at the injection well, and the samples were used to estimate the total mass and average concentrations of the organic constituents and dissolved oxygen in the injection water (Table 3.1). The total mass of chloride was not estimated from chloride monitoring of the injection water due to interferences at the time with the laboratory procedures. Instead it was estimated from the known chloride concentration in the injection water prior to additions (25 mg/L), and the mass of chloride (2.62 kg) added as sodium chloride. During the injection the concentration of the organics at the injection well slowly declined to approximately 75% of the initial concentration. This likely occurred as a result of sorption losses within the tubing and containers of the injection system. These losses do not affect the total mass estimates.

3.2 Sampling and Analysis

Multilevel piezometers were sampled with the sampling manifold described by Mackay (1985a). All organic solute samples were retrieved in 18 mL glass hypovials which were filled to the brim, poisoned with 0.1 mL of a 10% sodium azide solution, and then sealed with teflon-faced silicon septa leaving no entrapped air space. Sodium azide was only added during the second and subsequent sampling sessions after it was observed that total losses of all organic solutes could occur within 6 days in the vials at storage temperatures of 4°C. The manifolds were designed to provide duplicate samples from one of the sampling points. These were not true duplicates, however, because the two vials were filled sequentially from a piezometer tube, rather than each being filled from a split common sample.

For each sampling session, only a subset of the total network was sampled, based on estimated solute velocities and occasional sampling of selected piezometers between sessions. In all sessions, the observed plumes were encircled by piezometers in which no BTX and only background values of chloride were found.

For the first sampling session, all laboratory organic solute and chloride determinations for a given sampling point were made on the same water sample. This practice yielded inconsistent results for the chlorides due to chemical interferences by sodium azide and the small sample size, and in subsequent sampling sessions separate chloride samples were collected in polyethylene bottles. All organic samples were stored in coolers at about 4°C until analyzed.

Dissolved oxygen measurements were taken from selected multilevel piezometers immediately following each snapshot sampling session. The measurements were taken from alternate tubes of each chosen multilevel to provide a vertical cross-section of dissolved oxygen concentrations along the length of the organic and chloride plumes. All measurements were made in the field using the Winkler method, with syringes employed as reaction vessels.

Laboratory procedures are described by Patrick et al. (1985). The organic samples were solvent extracted within the hypovials using a modification of methods described by Mackay et al. (1985a) and Glaze et al. (1983). Detection limits were about 1 ug/L to 1.5 ug/L for each constituent. Chloride samples were anal-

ysed using an automated wet chemical procedure (Technicon Industrial Method No. 99-70 W/B) on a Technicon Autoanalyser II, and detection limits were about 1 mg/L.

Several measures were taken to evaluate the quality of the field concentration data (Patrick, 1986, Appendix B). Statistical evaluations were performed on field duplicate sample data, replicate data from a laboratory test of the peristaltic pump-manifold sampling technique, and replicate data from prepared laboratory standards that were analysed throughout the duration of the study. All three evaluations indicated that, with the exception of data from the first sampling session, the relative standard deviation for each of the organic solutes was about 5%. Field data for the first sampling session is considerably more variable because sodium azide was not added to samples at that time. The sampling technique introduced a slight negative bias to the organic sample data of -5%. The bias determined from the laboratory standards study was generally plus or minus 4% for each organic solute. Chloride results were generally better than the organic results for both variance and bias. The data are considered acceptably precise and accurate for use in evaluating the natural transport of the solutes.

3.3 Related Laboratory Studies

In addition to the field tracer study, several related laboratory experiments were conducted to further evaluate sorption, biological transformations, and the effect of spatial variations in hydraulic conductivity on solute transport.

In the sorption studies three small scale methods and a calculation procedure were used to determine retardation coefficients for benzene, toluene, and the xylenes in Borden sand. Included were static batch equilibrium experiments, dynamic laboratory column experiments, dynamic in situ column experiments, and calculations based upon regression equations relating the hydrophobicity of each organic solute to the organic carbon content of the aquifer material.

The biological transformation studies consisted of: 1) a preliminary investigation to quantify mass losses of the organic solute from hypovials during storage, 2) a more involved study to indicate the rate of mass losses through time, and the effect of various initial BTX concentrations, and 3) a qualitative study to identify transformation products. These studies were conducted in hypovials containing representative groundwater and sand. Such systems are termed microcosms as they are small-scale representations of natural systems.

In the preliminary transformation study a series of hypovials containing very similar initial concentrations of organic solutes in groundwater was incubated at $4^{o}C$, and pairs were analysed at various times to determine solute concentrations. The hypovials were filled with groundwater from a piezometer tube screened within the injected solute pulse, approximately three weeks after the injection. The results showed complete mass losses of all solutes within only six days incubation, which prompted the use of sodium azide as a solute preservative.

In the second transformation study hypovials were filled with both groundwater which had been spiked with organic solute, and a one gram innoculum of Borden sand. Sodium azide was added to some of the vials (as controls) prior to seal-

ing as a poison to inhibit microbial activity. Neither the sand nor the groundwater had been previously exposed to the organic solutes; the sand was obtained from a core taken from the site prior to the injection, while the groundwater was obtained from the same well used to supply injection water for the field study. The hypovials were analysed in triplicate at various times over an 80 day period for BTX concentration and dissolved oxygen concentrations were monitored by sacrificing selected vials throughout the study.

As part of this second study, microcosms of 25 g core material and sterile, BTX-spiked groundwater, purged of almost all oxygen, were established in 60 cm^3 hypovials and incubated at 10°C under anaerobic conditions. Organic concentrations were determined by repeated, periodic removal of 100 ul of water and analysis using High Performance Liquid Chromatography (HPLC). Procedures are described in Appendix A. Some microcosms contained sterilized soil and so were not microbially active and acted as controls to monitor BTX concentration losses due to volatilization and sorption.

In the third study to qualitatively assess possible products produced by the biological transformation of BTX, several 1 litre flasks containing 5 g Borden sand were filled with groundwater, spiked with the solutes, sealed, and then incubated at 10°C. At various times the flasks were removed from the incubator and poisoned with sodium azide, and then analysed by coupled gas chromatography/mass spectrometry for transformation products.

3.4 Data Management and Analysis

During the fourteen months following the injection, over 2300 samples were analysed, producing prodigious number of concentration data which were filed on computer, and then carefully cross-checked with laboratory gas chromatogram print-outs to ensure accuracy.

All mass estimates were made following corrections to the original concentration data, whereby adjustments were made to account for background of chloride (1 - 2 mg/L), introduced laboratory interferences for toluene (approximately 4 ug/L) and m-xylene (approximately 1 ug/L), interferences to benzene from contaminants in the hypovial septa, and sorption and diffusion effects at the polyethylene multilevel piezometers. Benzene interferences were eliminated after the first sampling session by boiling and baking the septa prior to use (Patrick et al., 1985). Laboratory experiments (Patrick, 1986) demonstrated that BTX could diffuse from groundwater outside polyethylene sampling tubing into the tubing and into the water standing within the tubing. Further, flushing the inside of the tubing with up to 20 volumes of water did not remove BTX to below detection. Such problems were confirmed by comparing the concentration data at the polyethylene multilevels with data at adjacent, unaffected teflon multilevels. Corrections to the polyethylene multilevel data were made by eliminating the suspect data points. The difference in estimates of the total mass of each organic solute, prior to and following the corrections, was generally 5% or less (Patrick, 1986).

It was desired to examine and compare the behaviour of each solute through time in terms of average velocity, total mass, and concentration distribution. This was achieved using the methodology of Freyberg (1985) to derive spatial

moment estimates for each solute concentration distribution at each sampling session time. The moments of interest are the zeroth, first, and second, which can be related, respectively, to the total mass (the basis for mass loss estimates), centre of mass (the basis for velocity estimation), and dispersion or shape of a solute concentration distribution. The estimates can be derived using the three-step methodology described in detail by Freyberg (1985):

1. data for each multilevel piezometer are vertically integrated using trapezoidal quadrature to derive a mass sum value for each solute at each horizontal (x,y coordinate) piezometer location.

2. the vertically integrated data are interpolated to a regular grid (grid nodes were spaced at 0.3 m intervals for the present study) using the interpolation routines in the Surface II Graphics System package of Sampson (1978).

3. an areal numerical quadrature routine which sums the integral of non-overlapping unit cells is applied over the grid of values to derive the moment estimates.

Using the Surface II package, two-dimensional contour plots are produced from the interpolated grid of vertically integrated concentrations. The contours are produced following a linear interpolation between grid points, and are then smoothed using an internal Bessel function routine. The final plots provide a visual presentation of the general solute behaviour, although the vertical distribution of the solutes is masked. The units are mg.m. L^{-1} and are essentially the mass per square unit of surface area. Zero-solute concentration contours are not produced and the reader is cautioned not to infer an edge or limit of the plumes from the resultant figures.

A modified approach was required to deal with the results of sampling in 1985. The newly-installed multilevel piezometer network was sampled on eight occasions from August 29 to October 17 and sporatic occurrences of benzene were found. On any ocasion no more than 7 samples contained detectable (>1.8 ppb) benzene and the maximum benzene concentration found was 135 ppb. On the last sampling, no benzene was detected. In order to estimate the total mass of benzene, it was assumed that the sporatic occurrences represented discrete water masses containing benzene. The location of each water mass was projected to its location on September 18 (day 406) assuming a benzene velocity of 7 cm d^{-1} in a direction consistent with Figure 4.2b and no mass loss. The phantom sampling network with its benzene concentrations were treated in the manner described above in order to derive the zeroth moment or total benzene mass. The result is considered much less precise than mass estimates for previous snapshots.

It was expected that the methodology would introduce some degree of bias to the moment estimates. An exploratory study (Patrick, 1986, Appendix E) was conducted to estimate the bias by applying the methodology to a fictitious plume generated using a two-dimensional analytical solution to a point source input of an ideal tracer (Freeze and Cherry, 1979, pg. 395; Carlslaw and Jaeger, 1959, pg. 258). Different piezometer spacings were used in conjunction with various interpolation functions available with the Surface II package to generate grid matrices, and the moment estimates were then evaluated and compared with known values. It was found that the grid matrices often contained small background values which

were inadvertently introduced by the interpolation routines. These required elimination prior to estimating the moments. Results of the study suggested that, for a plume of a comparable size and monitored density to that at the field site, the methods introduce a slight negative bias to the mass estimate (zeroth moment), a robust response for the centre of mass estimate (first moment), and a variable response for the variance estimates (second moment). The negative bias in mass was reduced to approximately -5% when either the inverse distance to the sixth power or the constrained inverse distance squared weighting options were used. Increasing the density of the piezometer network reduced the variability of the moment estimates, as expected.

In applying the methodology to the field data for chloride, a similar trend in bias for the mass estimates was observed. Using the constrained inverse distance squared weighting options consistently yielded the highest total mass values and this option was therefore used throughout the study for all data sets, including those for the organic solutes.

Chapter IV

RESULTS

4.1 Field Experiment - Horizontal Transport

A horizontal two-dimensional illustration of the behaviour of the chloride, benzene, and toluene plumes during transport is presented in Figure 4.1. Shown are contours of the solute mass distribution at 3, 53, and 108 days after injection. As described in section 3.4, the plots are constructed from vertically integrated concentration values using the Surface II contouring package of Sampson (1978). These values represent the total mass of solute.

At day three the plume shape is essentially the same for all solutes, being somewhat circular and slightly down-gradient of the injection well. Also illustrated in Figure 4.1 is an apparent bimodality or dual maxima in the distribution of mass about the plume centre which may be related to a non-uniform input of solute concentrations during injection, heterogeneities of soil properties near the injection well, or an artifact of the contouring routine.

At later times during migration the chloride plume elongated only in the direction of groundwater flow, indicating significant longitudinal dispersion but little lateral dispersion. This behaviour is consistent with the results of previous tests of dispersion in the Borden study area (Mackay, 1985b; Sudicky et al., 1983). The organic solutes did not elongate to the same extent as chloride, but rather shrank in size indicating a significant loss of dissolved mass. The size reduction is clearly evident for toluene, which shows no elongation through time.

Trajectories of the plumes were determined from the first moment estimates for the centres of mass (Figure 4.2). All of the solutes followed a similar path in three distinct flow directions, with chloride travelling the furthest, followed by the organic solutes. Causes for the directional changes are not clear. They may have resulted from changing groundwater gradients or from encounters of the plumes with layers of different hydraulic conductivity. After the first sampling session, gradients were not measured at the site in sufficient detail to discern small scale changes. However, groundwater gradients are known to oscillate seasonally at the site (Table 2.1) with estimated changes in direction of approximately 13° over the year.

Figure 4.3 indicates the approximate trajectory for benzene over the total 406 day experiment. It appears that the trajectory became more similar to that of the previous experiment at this site (Mackay et al., 1985b) after about 265 days. The centre of mass for day 265 is very imprecise. It is taken at the only piezometer which BTX (only benzene) was detected. The centre of mass for day 406 was selected by visual examination of the inferred benzene mass distribution obtained by integrating the September - October 1985 results as previously described.

Figure 4.1: Contour plots of vertically-integrated concentrations showing chloride, benzene and toluene plumes at 3, 53, and 108 days after injection. Units are mg.m. L^{-1}.

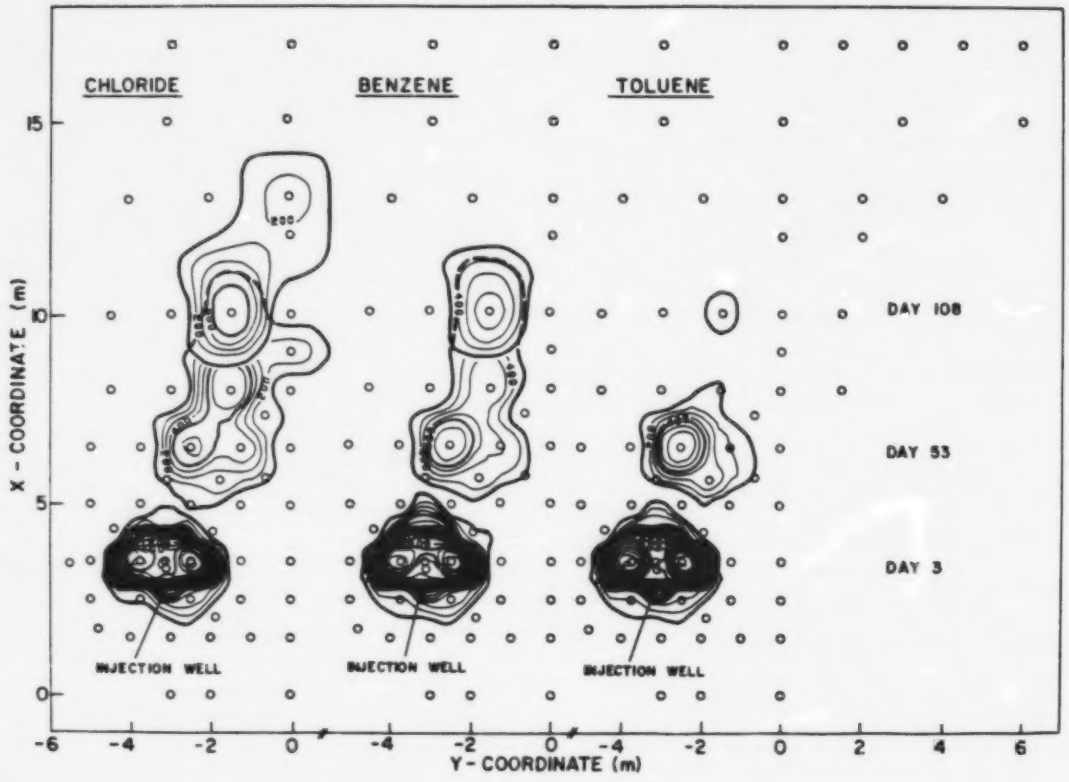


Figure 4.2: Trajectories of the centre of mass of the solutes until 108 days after injection

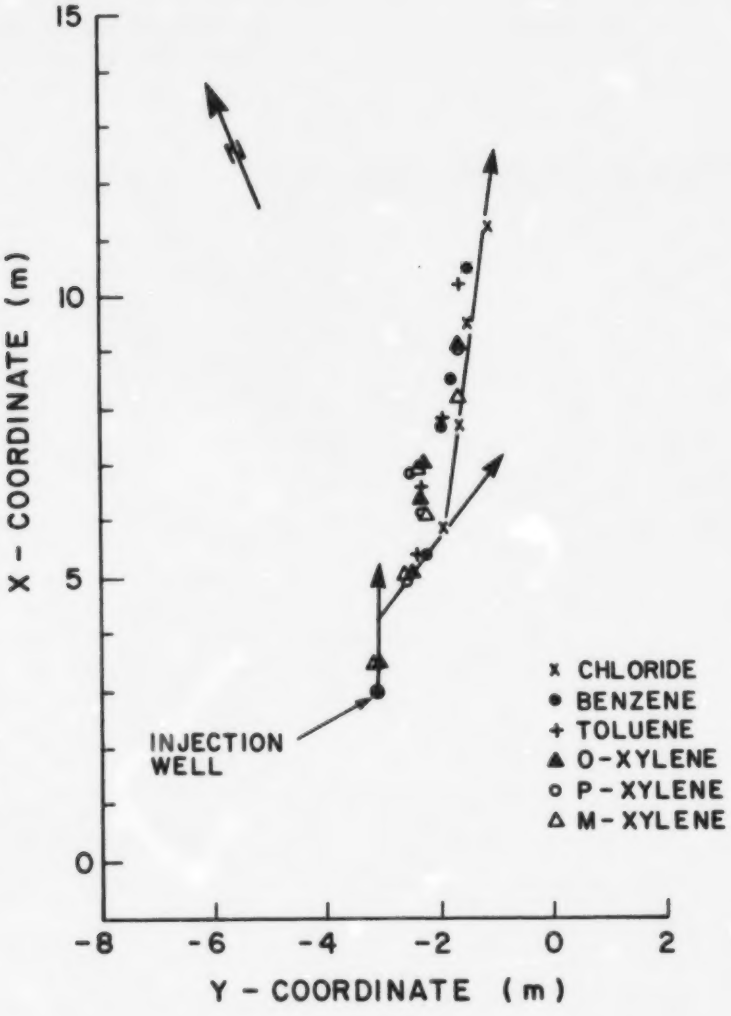
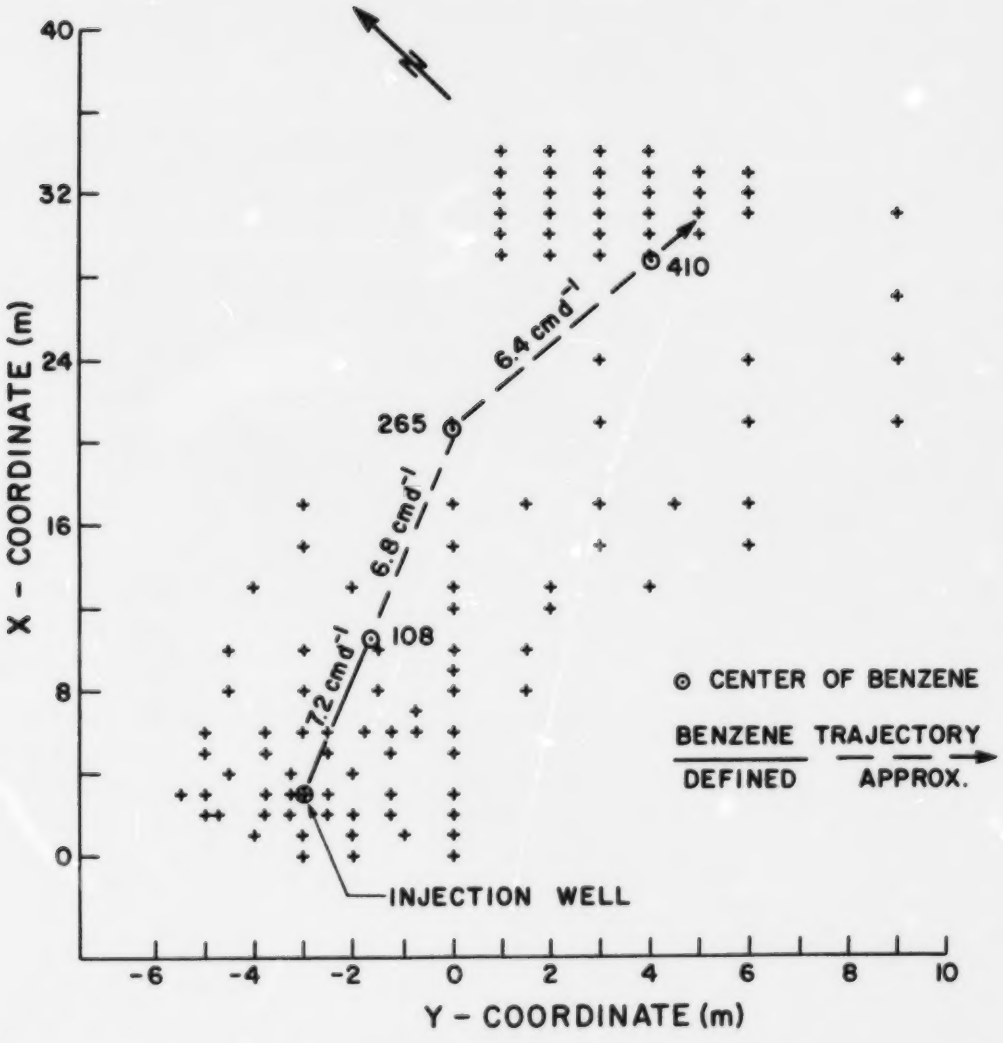


Figure 4.3: Variation in the trajectory and horizontal velocity of the centre of mass of benzene over 410 days



The magnitude and direction of the chloride velocity, calculated between snapshots, is presented in Table 4.1. Since the chloride behaves conservatively, its velocity should reflect the actual groundwater velocity along the flow path. The velocity was initially about 0.09 m/d and declined to about 0.07 m/d in the latter half of the study. The decline was not related to the hydraulic effects of the injection, which had been shown to be completely dissipated prior to the first sampling session. It may have resulted from changing groundwater gradients and/or from a decreasing hydraulic conductivity along the flow path.

Table 4.1: **Velocity of the Chloride Tracer**

Period	Velocity		Distance
	Magnitude(m/d)	Direction	Travelled(m)
Day 3-Day 32	0.093	N46°E	2.71
Day 32-Day 53	0.089	N30°E	1.87
Day 53-Day 81	0.063	N25°E	1.77
Day 81-Day 108	0.067	N32°E	1.80
Day 3-Day 108	0.078	-----	8.15

4.2 Field Experiment - Vertical Solute Distribution

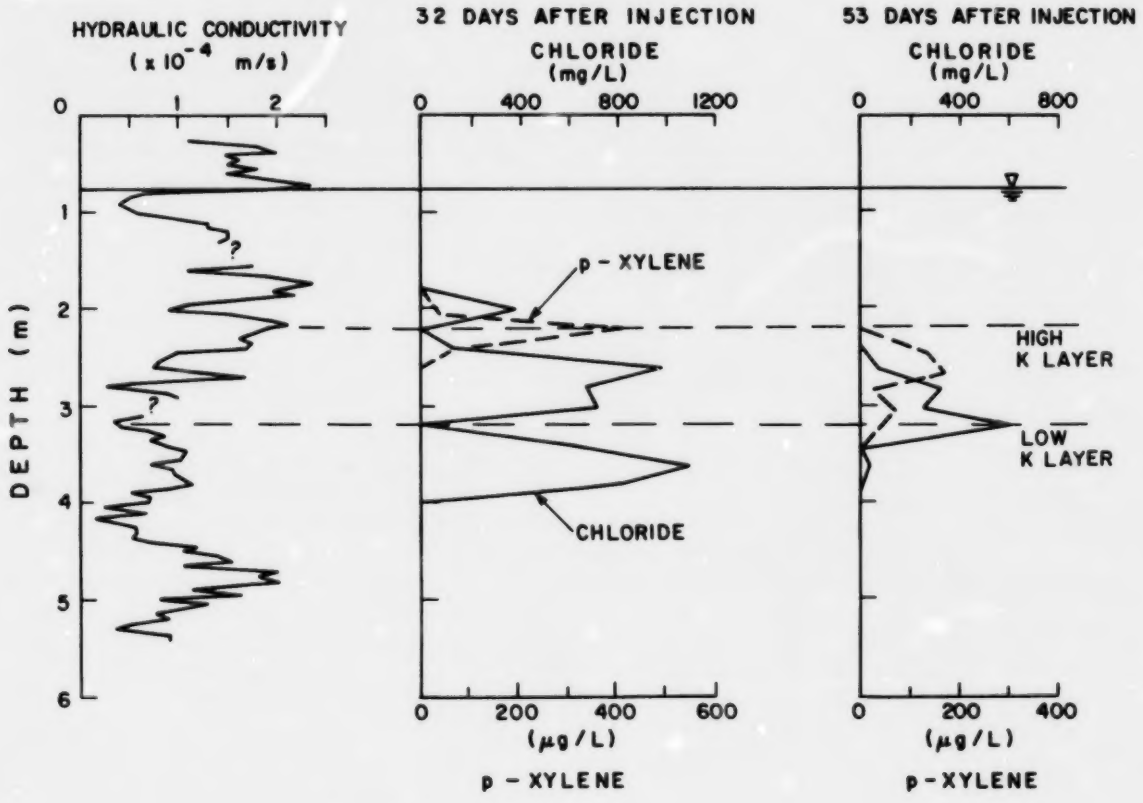
Following the injection the vertical distribution of the solutes assumed very similar shapes. They display the same type of erratic but highly correlated vertical profiles observed as an initial condition for a previous injection experiment at the site (Figures 6 and 7 of Mackay, 1985b).

The solute distribution at later times was examined in detail at a single multilevel piezometer located approximately 3 m down-gradient of the injection well (Patrick and Barker, 1985). Prior to installation, an undisturbed core sample had been retrieved and hydraulic conductivity measurements were made on the core using the method of Sudicky (1985).

Vertical profiles of the chloride concentration and the concentration of one of the more retarded species, p-xylene, are presented in Figure 4.4 together with the vertical hydraulic conductivity profile. Variations in hydraulic conductivity reflect the thin horizontally layered structure of the sand. The concentration profiles shown are constructed from a sampling interval of 0.2 m while the vertical scale of the layered structures is approximately 0.1 m (Sudicky, 1985). The concentration profiles may therefore incorporate some smoothing. It is apparent from Figure 4.4, however, that a correlation exists between the concentration distributions and specific layers of aquifer sand. Layers range from (2×10^{-4} m/s) to low (0.5×10^{-4} m/s) conductivity. In each layer chloride first enters the profiles and is followed at a later time by the retarded species (e.g. p-xylene). Because the layers have differing values of hydraulic conductivity, the overall effect is to produce an apparently erratic distribution of solutes.

The erratic concentration profiles should, according to Gillham et al., (1984), become smooth with time as a result of the vertical diffusion of constituents from layers of high to low concentration. At the Borden site diffusion appears to be the primary vertical dispersion mechanism (Sudicky, 1983). Smoothing was not observed in the present study after travel distances of over 7 m and times of four months. Longer times may be necessary for smoothing to become noticeable. Additionally, the sampling for benzene around day 406 (27 m travel distance) found very erratic benzene distributions. This suggests that a mass loss mechanism such as biodegradation may maintain an erratic concentration distribution even for long travel distances.

Figure 4.4: **Vertical profiles of hydraulic conductivity (K) and the concentration of chloride and p-xylene at a single multilevel piezometer**



4.3 Field Experiment - Mass Estimates

4.3.1 Chloride

Because chloride is known to behave as a conservative and non-reactive tracer at the site, a comparison of the estimates of the chloride mass through time with mass inputs provides a useful means to evaluate the efficacy of the overall methodology used in this study. The mass estimates determined for each snapshot session for chloride and the organic solutes is presented in Figure 4.5.

The mass of chloride initially injected was 2.30 kg. As indicated in Figure 4.5, the mean value for chloride from the field snapshot data was only 1.80 kg. The moment estimation procedure may introduce a negative bias to the mass estimates. Other causes are speculative, and may include inadequate spatial sampling of the plume due to limited piezometer density, or a possible error in measuring the input mass of chloride. Laboratory methods were shown to have an insignificant degree of bias on the chloride results, and estimates of mass removal due to sampling indicated that no more than two percent of the mass had been removed in total.

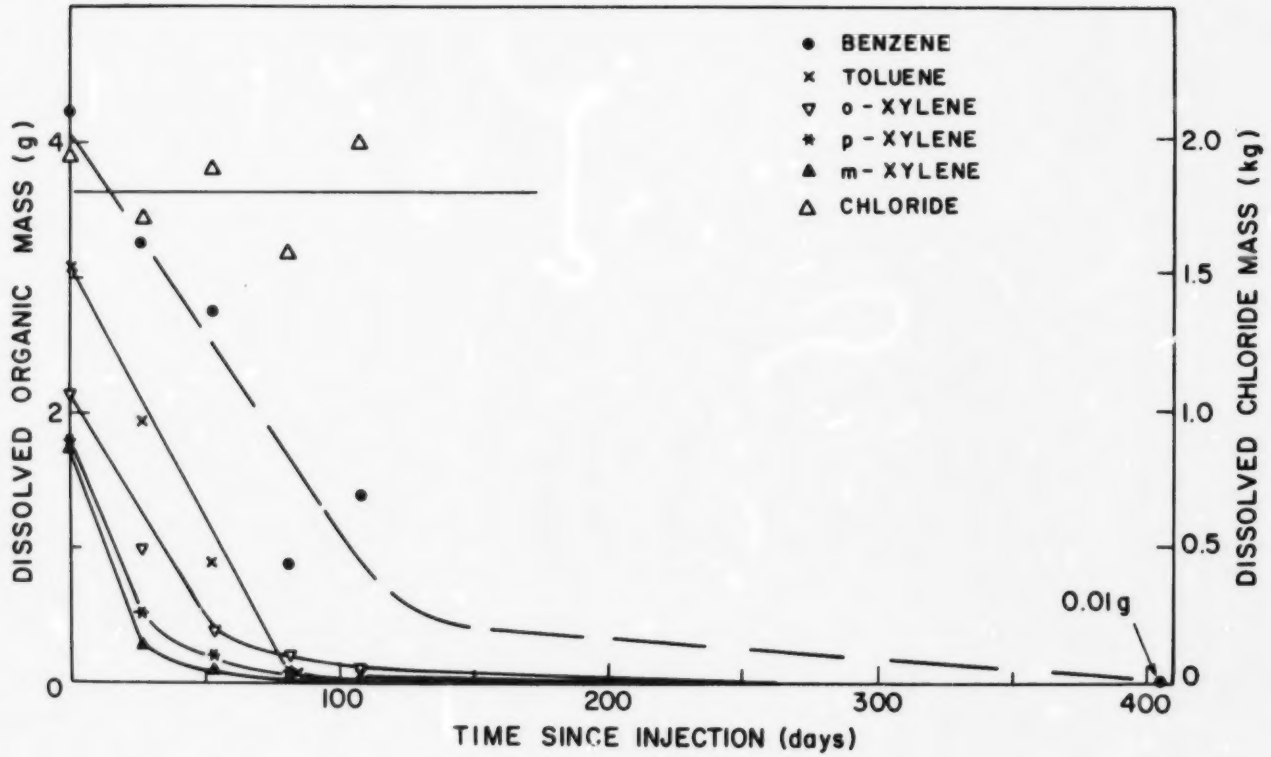


Figure 4.5: Estimates of the total dissolved mass of the chloride and organic solutes remaining in the groundwater up to 406 days after injection.

4.3.2 Organic Solutes

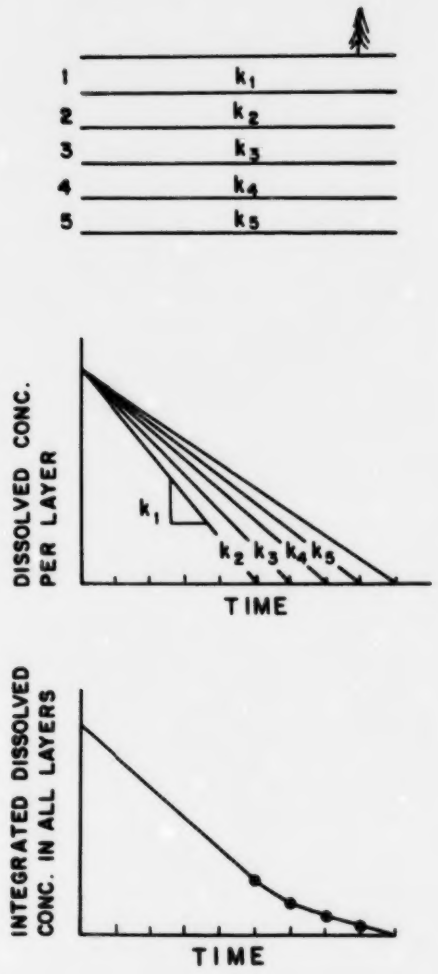
The dissolved masses of all the organic solutes as a function of time are also shown in Figure 4.5. The overall estimates are probably negatively biased, as was demonstrated for chloride, although the magnitude and particularly the variance of the biases are likely different because of the different, and generally lower piezometer density relative to the plume size at later times. The low piezometer density is a consequence of the extensive mass losses, as illustrated in Figure 4.1 for toluene, where essentially only two multilevel piezometer intercepted the remaining plume by day 108 and of these, only one intercepted the bulk of the plume. The benzene mass at day 406 is only approximate, as previously mentioned. In any event, a plot of the masses through time (Figure 4.5) illustrates some potentially significant trends: 1) The loss of mass rate for each organic solute appears to be initially constant through time followed by a distinct tailing (rate reduction) as the mass is reduced, and 2) The rates of mass loss are initially very similar.

An initially constant rate of mass loss suggests that the reaction or process is zero order, wherein the rate of mass removal proceeds in a manner independent of the concentration of the solutes. Zero order rates have been proposed in the past as simplifying assumptions to describe the "in situ" transformation of petroleum hydrocarbons (Vanlooke et al., 1975). However, in the present case a constant mass loss rate does not necessarily imply a zero order reaction with respect to concentration, because the plume size, and hence the volume of groundwater containing the dissolved solute changes with time. A zero order reaction would only yield a constant total mass loss rate if the plume remained essentially the same size through time. By similar reasoning, the reaction rate could be first order or higher, and still yield apparently constant total mass loss rates because of the changing size and configuration of the plumes. This problem is expanded upon by Patrick (1986).

The tailing of the mass curves suggests an overall first order reaction. Tailing is also consistent with biotransformation processes in which threshold concentrations (Alexander, 1985) or minimum substrate concentrations are reached (McCarty et al., 1981), below which mass losses do not occur, or occur at reduced rates due to cemetabolism. Preliminary laboratory evidence suggests that a threshold concentration may exist, which may account for the tailing effect.

An alternative explanation of the tailing is related to the layered structure of the aquifer sand, and consequently to a layered heterogeneous distribution of those factors which determine mass removal rates. It can be hypothesized that different rates of biodegradation occur in different soil layers, as illustrated in Figure 4.6, related to a heterogeneous distribution of the numbers and kinds of soil microorganisms or of the limiting nutrients. These rates may be zero order, as shown in the figure, or of a higher order. At early times removal is effected in all layers producing an overall uniform rate of mass loss. However, as the substrate is removed or the nutrients depleted from particular layers, then these layers no longer contribute to the total mass loss. In other words, as the organics are removed from the layers having the highest rates, mass loss occurs only in the layers with slowest mass loss rates in which organics are still present. Thus the overall mass loss rate declines over time, producing tailing of the mass versus time curve. Field evidence suggests this occurs, with heterogeneously-distributed dissolved oxygen behaving as a limiting nutrient.

Figure 4.6: Mass loss rates for a hypothetical layered system where zero order reaction kinetics operate.



Zero order rates of overall mass removal were estimated from best fit lines placed through the linear portion of the curves in Figure 4.5. The rates, presented in Table 4.2, should be regarded as order of magnitude estimates in light of the expected variance and bias of the data. They are very similar, as one would expect, because the compounds themselves are structurally very similar and have similar chemical properties. The order of the mass removal rates, indicated as follows, is also somewhat predictable:

Benzene < o-xylene < toluene < p-xylene < m-xylene

As an initial step in the bacterial transformation of benzene, cleavage of the ring is required whereas the initial transformation of the methylated benzenes (toluene and xylenes) can proceed by either ring cleavage or oxidation of a methyl group (Gibson, 1984). Therefore, one could predict that the methylated benzene would be more readily transformed than benzene in the presence of a mixed consortium of microorganisms. o-Xylene is the more recalcitrant of the xylenes to biotransformation, likely because of the close proximity of the methyl groups on the ring. Only recently have bacteria been isolated which can use o-xylene as a sole carbon source (Gibson, 1984). Its transformation likely proceeds in nature as a result of cometabolism in the presence of other similar hydrocarbons (Jamison et al., 1976). The transformation of o-xylene would therefore likely proceed more slowly, as was observed.

The prolonged persistence of benzene (no other organic solute was detected on or after day 265) reflects, in part, its relative recalcitrance. However, the extended persistence also reflects limited oxygen availability, since benzene has been shown in laboratory studies, described in the next section, to be more quickly biotransformed to below detection when oxygen is available.

Table 4.2: Estimated Zero Order Mass Removal Rates

Solute	Initial Dissolved Mass Estimate* (g)	Dissolved Mass Remaining by Day 108 (g)	% Removal	Zero Order Rate ** (mg/d)
Benzene	4.17	1.35	68	-30
Toluene	3.04	0.08	97	-37
o-Xylene	1.75	0.06	97	-33
p-Xylene	1.75	0.01	99	-47
m-Xylene	2.14	0.11	95	-55

* estimates do not include mass sorbed onto aquifer solids
** estimated from linear portion of mass loss curves (Figure 4.5

4.4 Laboratory Biotransformation Studies

The results of the field experiment alone are not sufficient to attribute the mass losses of the organic compounds to any particular process. However, of the possible alternatives which can be considered, biotransformation is favoured as the likely removal mechanism. The BTX compounds are naturally occurring and have many natural analogues in the environment which can be completely biodegraded (Hopper, 1978). Numerous laboratory studies have shown that the BTX compounds, in the presence of molecular oxygen, can be readily transformed by a variety of microorganisms in groundwater (Kappeler and Wuhramann, 1978; Jamison et al., 1976), seawater (Button et al., 1981; Van Der Linden, 1978), subsurface soil (Wilson et al., 1983), and sea and lake sediments (Horowitz et al., 1982; Ward et al., 1980). Limited field evidence also implicates biotransformation as an aerobic removal mechanism of mono-aromatic hydrocarbons (Borden et al., 1984; Schwarzenbach et al., 1983).

In the present field study, aerobic regions were found within the solute plumes during all sampling sessions. The measured dissolved oxygen concentration was never less than 0.2 mg/L, although anoxic zones or microsites within the aquifer were possible. Because the biotransformation of BTX solutes at significant rates requires molecular oxygen (Gibson, 1984), this process was probably active within the aquifer. Alternative mass removal mechanisms such as volatilization, chemical transformation, or sorption are unlikely. Volatilization losses were prevented since the solutes remained below the water table throughout the study. Chemical transformations of BTX compounds were not observed in microbially-inactive laboratory experiments using Borden sand and groundwater. Sorption of the BTX solutes by the aquifer sand is a weak and generally reversible process (Ptacek et al., in press). Mass removal by sorption, as an alternative mechanism, would require a strong, irreversible process which has never been demonstrated for the Borden aquifer. Although this possibility was apparent in initial laboratory retardation experiments (Patrick et al., 1985) subsequence batch and column studies recovered almost all of the BTX when a bacteriacide, sodium azide, was employed. These studies will be described in detail in a future PACE report.

Exploratory laboratory studies were conducted to assess the biotransformation of the BTX solutes (at concentrations similar to that of the injection) using Borden groundwater and sand. Groundwater from the well which provided the injection water was spiked with organics dissolved in methanol and added to 60 cm^3 hypovials containing 1 g of Borden sand obtained from a core which was cut and sampled aseptically. The hypovials were immediately capped with teflon-faced septa and sealed by crimping. These hypovial "microcosms" were then incubated at 10°C. Controls were established as above, but with the addition of 0.1 cm^3 10% sodium azibiode to inhibit BTX degradation. At various times over 80 days, three active microcosms and one control were analyzed for BTX by the micro-extraction procedure described by Patrick et al. (1985). Also, one active microcosm was analyzed for dissolved oxygen content using a modified Winkler titration technique.

Figure 4.7 shows the change in organic concentrations over time for controls and active microcosms with initial BTX concentrations similar to the injection concentration. The changing dissolved oxygen concentration is also indicated. Points represent the average of triplicate analyses for organics and single analyses for oxygen.

Experiments generally showed a lag period of 3 to 6 days prior to the onset of biodegradation. The solute concentrations then declined at near constant rates until either the detection limit was reached (1 to 2 ug/L) or until a point where tailing occurred and the rates declined. In all cases, BTX concentrations declined to below detection. Hypovial controls, which had been poisoned with sodium azide, showed no concentration change through time.

Dissolved oxygen was almost always found in the hypovials (see Figure 4.7). Because the solute concentrations were generally sufficient to have depleted the oxygen supply via biodegradation, oxygen is presumed to have entered the vials by diffusion through the hypovial septa. It is therefore possible that the tailings of concentration declines could indicate that the rate-limiting process was diffusion into the hypovials rather than the metabolic rate when oxygen is not limiting.

Estimated rates of transformation (mass loss) were calculated from the linear portion of the concentration versus time curves generated from an experiment conducted at $10^{o}C$. Results (Table 4.3) similar to those estimated from the field study were found.

Figure 4.8 indicates the changing concentrations of BTX over 60 days, when 3.0 mg/L each of benzene, toluene, and o- and m-xylene were spiked into microcosms incubated anaerobically. For all organics, greater concentration decline occurred in active microcosms than in sterile controls, but almost all of this decline occurred witn 14 days, after which time little decline is apparent. This initial decline is attributed to sorption (as seen by decline in sterile controls) and to aerobic biotransformation. The anaerobic incubation prevented oxygen leakage into the microcosm as occurred in the above-mentioned experiments. This seems to have greatly inhibited BTX biotransformation (Figure 4.8). It is concluded that anaerobic biotransformation is very slow - essentially zero in the time-frame of these experiments.

A second series of experiments were conducted with similar proportions of BTX but with total BTX concentrations ranging from about 0.40 to 15.1 mg/L and initial dissolved oxygen concentrations of both 2-3 mg/L and 6-8 mg/L. In part, these experiments were conducted to evaluate possible toxic effects of high-BTX levels and to evaluate the effect that higher BTX concentrations had on the rates of biotransformations. Representative results of two such experiments are shown in Figures 4.9 and 4.10.

At concentrations similar to the field study (Figure 4.7), the initial mass loss rates were similar for the aromatics and followed a 6 day (about) lag period. In this experiment all xylenes were below detection by day 42 while small concentrations of benzene (17 ppb) persisted on days 42 and 64, and similarly, small concentrations of toluene (8-10 ppb) also persisted on these days. Although dissolved oxygen levels have dropped from almost 8 mg/L to about 1 mg/L, oxygen is still apparently present and so its rate of leakage or diffusion may not be controlling the BTX mass loss rate. This suggests that either some other nutrient has become limiting for biotransformation or that a threshold level has been reached beyond which the biotransformation mechanism changes and a much slower mass loss reaction occurs.

With higher initial BTX concentrations of 15.1 mg/L (Figure 4.10), m- and p-xylene (not shown) go to below detection (2 ppb) on day 64, while 30 to 700 ppb

Figure 4.7: Changing concentration of organics and oxygen in representative microcosms.

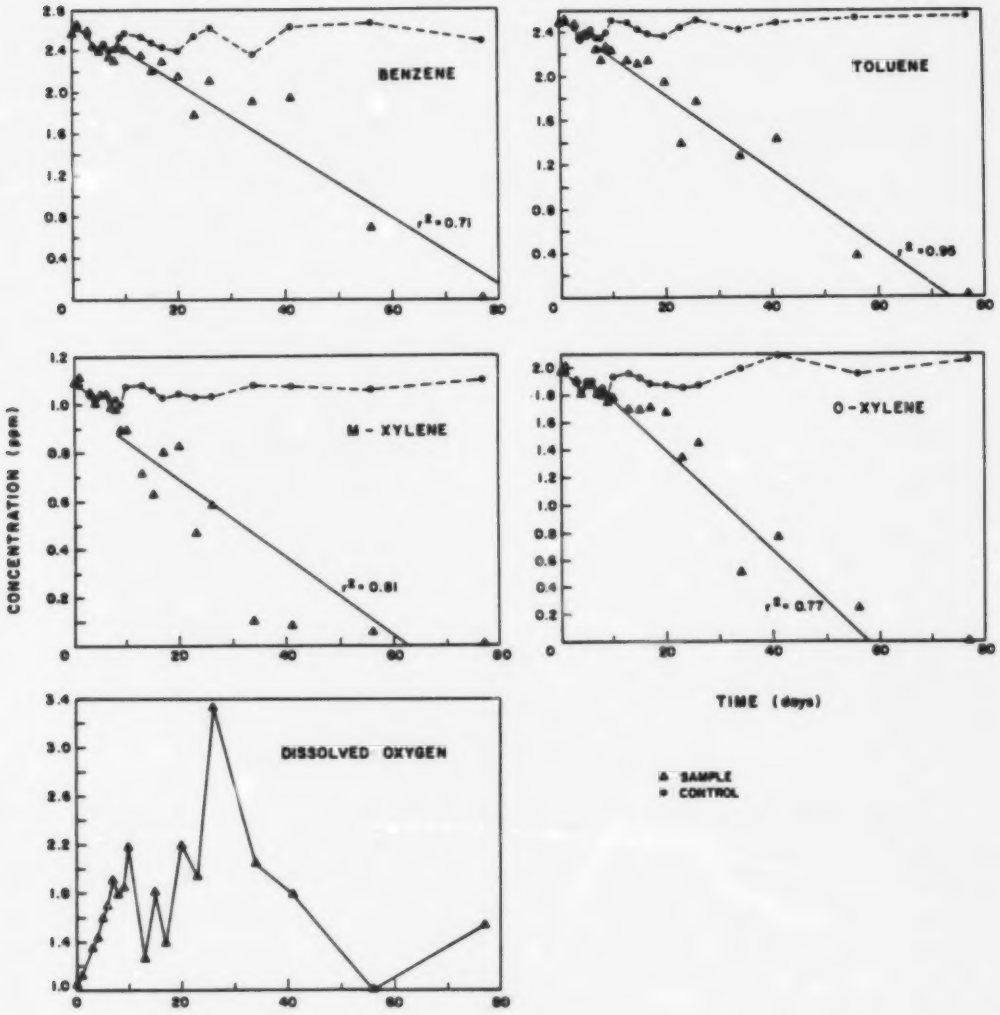


Table 4.3: **Laboratory Transformation Rate Estimates**

Solute	Initial Concentration (ug/L)	Day 77 Concentration (ug/L)	% Removal	Zero Order Rate* (ug/d)	Rate in 2000 L (mg/d)
Benzene	2570	16	99	-32	-64
Toluene	2490	22	99	-34	-68
o-Xylene	1971	7	>99	-30	-60
m-Xylene	1090	5	>99	-28	-56

* estimated from linear portion of concentration-time curves

Figure 4.8: **The change in BTX concentrations in microcosms of Borden sand and groundwater under anaerobic conditions. Initial concentrations are 3.0 mg/L of each organic.**

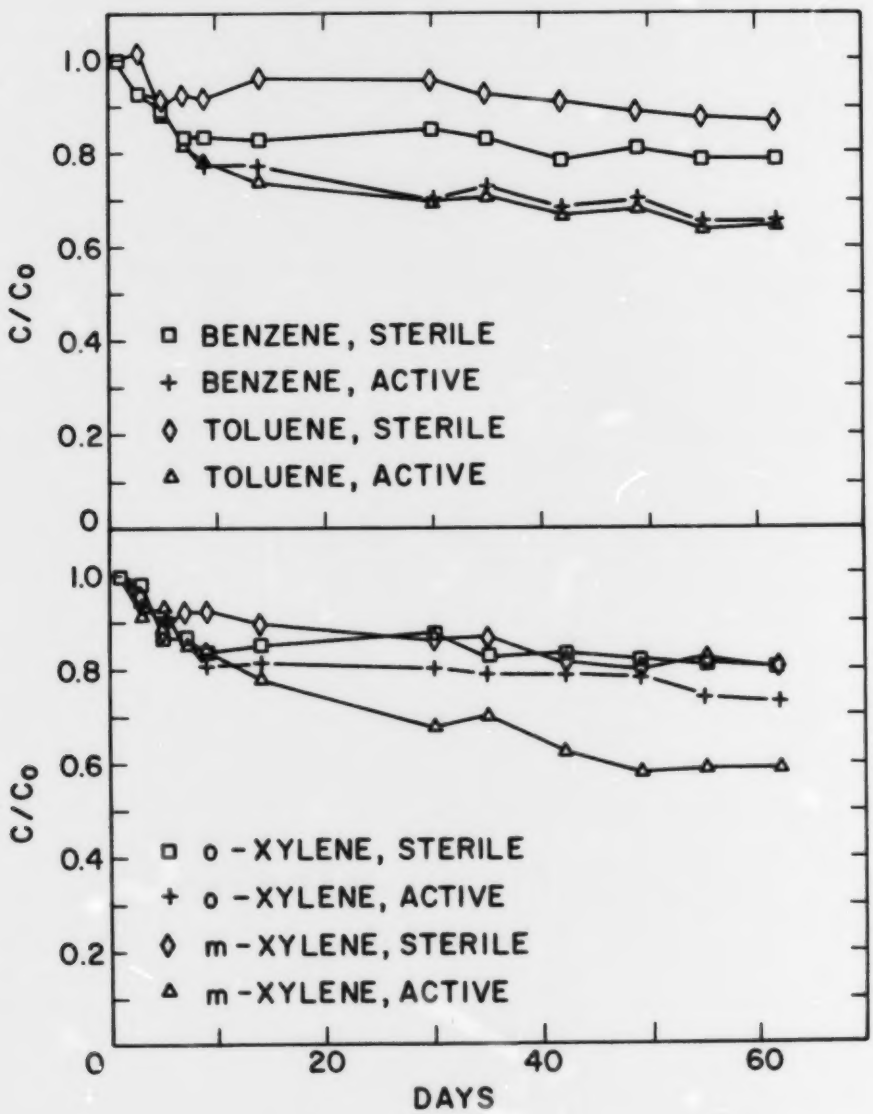


Figure 4.9: The decrease in benzene, toluene, o-xylene and oxygen concentrations in microcosms of Borden sand and groundwater. Initial, total BTX is 5.35 mg/L.

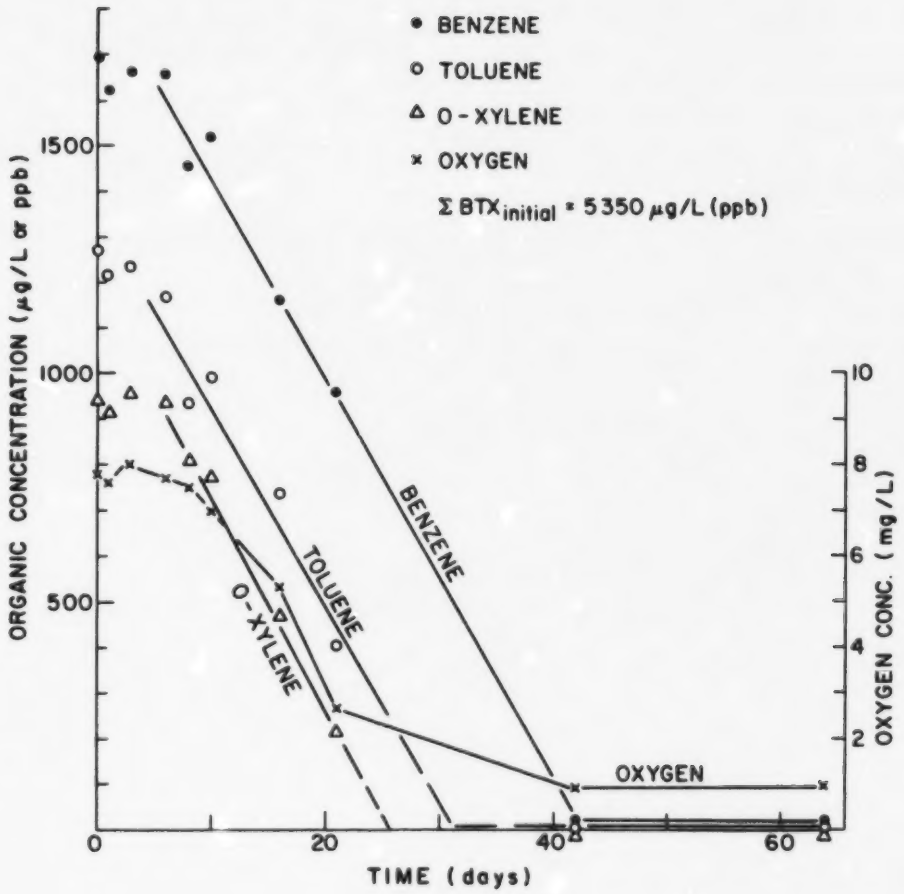
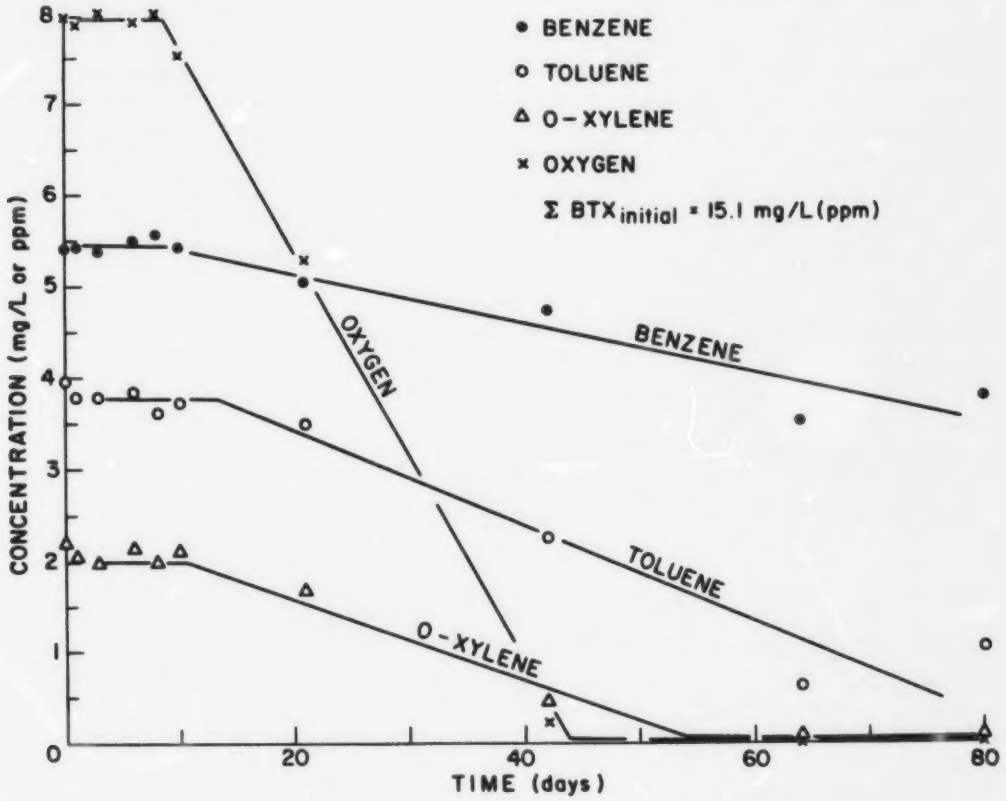


Figure 4.10: **The decrease in benzene, toluene, o-xylene and oxygen concentrations in microcosms of Borden sand and groundwater. Initial, total BTX is 15.1 mg/L.**



o-xylene persists, and much higher concentrations of benzene and toluene also persist. A dramatic decrease in dissolved oxygen is observed following the 8 to 20 day lag before the onset of major biotransformation. As with previous microcosm experiments in hypovials, the oxygen required by the observed BTX mass declines exceeds that initially present. For an initial 1 mg O_2/L, only about 0.16 mg BTX/L can be consumed assuming a simple mass balanced reaction as:

$$C\ 7.15\ H\ 8.30\ (BTX) + 18.45\ O_2 \rightarrow 7.15\ CO_2 + 4.15\ H_2O$$

Thus for the experiment shown in Figure 4.8, the removal of about 5.3 mg BTX/L would require 33 mg O_2/L, well beyond the 7-8 mg O_2/l available initially. It appears that the septum cap is permeable to O_2, and that the initial oxygen present in the microcosms is augmented by diffusion or leakage of O_2 into the hypovial during the experiment.

Because of this leakage of oxygen into the microcosms and because the BTX transformation may be limited by oxygen-availability, it is not reasonable to evaluate the rates of BTX decrease in these experiments as representative rates of aerobic (or anaerobic) biotransformation. Mass loss rates may simply reflect rates of diffusion or leakage into the hypovials. For example, the similar benzene mass loss rates represented in Figures 4.9 and 4.10 (about 1.5 mg/L in 40 days) probably reflects the similar rates of O_2 diffusion into the hypovials and should not be used to infer an essentially concentration-independent biotransformation rate.

It is clear, however, that even high concentrations of BTX does not inhibit BTX biotransformation. The suggestion of a threshold of 10-20 ppb BTX (Figure 4.9), below which benzene and toluene mass loss rates become much smaller is not supported in the field study. Even after 81 days, and more obviously after 406 days, persistent benzene does not occur as a plume at 2-20 ppb levels, but rather occurs in very few points and at sporatic, and sometimes high (100 ppb) levels. Also in other laboratory experiments not shown in Figures 4.9 and 4.10, benzene levels usually dropped to below detection (2 ppb) within 64 days.

In another laboratory study, several products of BTX biotransformation were identified using coupled gas chromatography/mass spectrometry. Phenol was found to slowly accumulate during the study. Other products which were identified but did not exhibit any particular trend through time were two methyl phenols, two dimethyl phenols and o-toluic acid (2-methyl benzoic acid). The methylated phenols were not differentiated into specific isomers because of mass spectral similarities. All of these products have been identified in other studies as compounds which may form during the transformation of BTX (Gibson, 1984, and references therein). Phenol, unlike the other products, is believed to form from the oxidation of benzene by eucaryotic organisms, and not by the procaryotes (bacteria). Analysis of about 8 groundwaters from the field plume did not identify any of these transformation products. Detection limits have not been defined, but are probably 5 to 10 ppb for these compounds.

The results of the biotransformation studies, although exploratory, further implicate biotransformation as the cause of the mass losses observed in the field. Oxygen appears to be required for significant biotransformation to occur. It is of interest and concern that phenol may be produced in groundwater thereby creating an additional contaminant which is mobile in sandy aquifers (Sutton and Barker, 1985). Perhaps in the field experiments the oxidation rate of the products is more

rapid than the initial biotransformation step of the BTX and the products only accumulate under oxygen-limiting conditions.

4.5 Dissolved Oxygen

Because of the importance of molecular oxygen in the biotransformation of BTX, dissolved oxygen concentrations were examined during the injection experiment in detail along a vertical section of the expected flow path of the solutes. Prior to injection the dissolved oxygen profile appeared layered (Figure 2.1) with a predominant band of low dissolved oxygen bearing water "sandwiched" between layers having a higher concentration. It is perhaps coincidental that the low dissolved oxygen band corresponds very closely with the high conductivity layer illustrated in Figure 4.4.

During the injection, the injection water had a lower dissolved oxygen concentration than the displaced *in situ* groundwater. The BTX concentrations injected were sufficient that oxygen was expected to become limiting as biotransformation proceeded. Although anoxic zones within the plumes were never confirmed during the study, it is likely that anoxic zones or sites were produced by oxygen consumption during BTX transformation.

An approximate outline of the low dissolved oxygen zone at 32 days after injection, and the limits of detectable benzene and p-xylene at 26 days are presented in Figure 4.11. Because the dissolved oxygen measurements were taken at larger vertical intervals than the organic solutes, and at later times, the results are not precisely comparable. However, the effects of several potentially important processes are evident:

1. Benzene, being the more mobile of the organic solutes, leads the p-xylene.

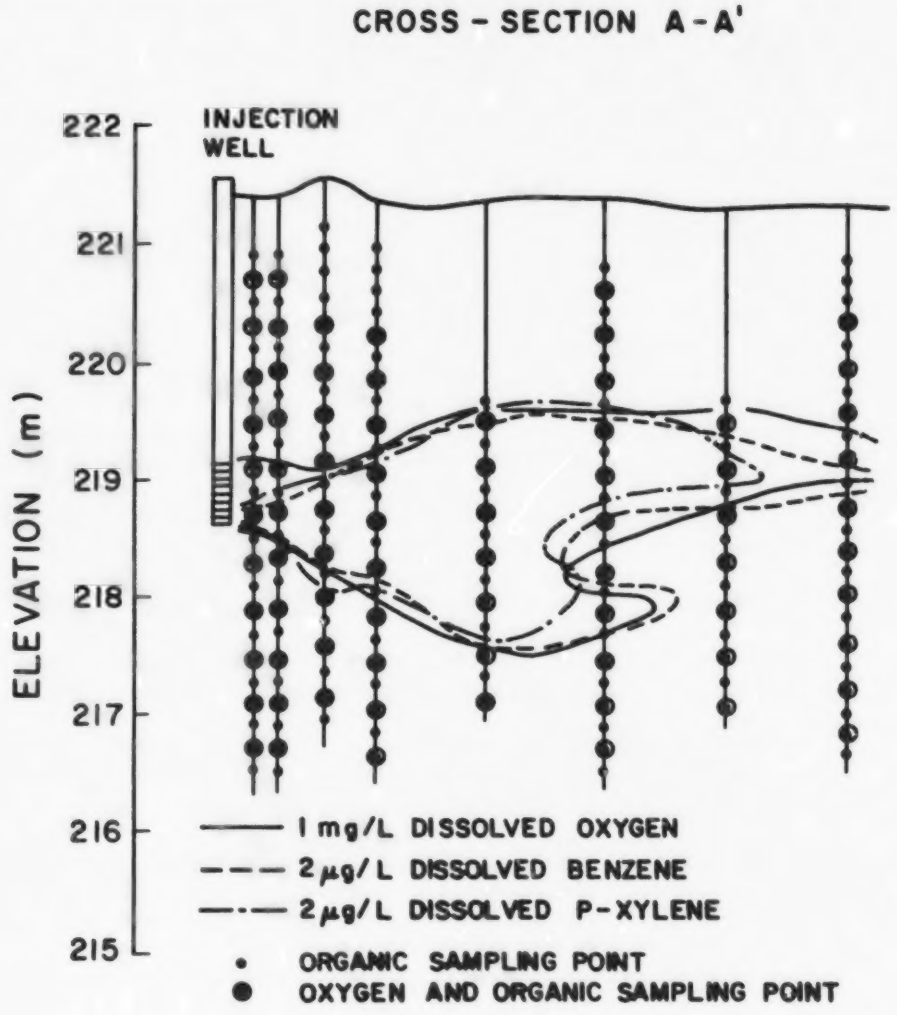
2. The low dissolved oxygen "plume" apparently is not retarded as it overlaps the benzene and consequently is leading the p-xylene.

3. The fingering in the upper portion of the plumes corresponds closely with layers of high hydraulic conductivity (Figure 4.4) and low dissolved oxygen (Figure 2.1).

The relative velocities of the organic solutes in relation to the advance of the low dissolved oxygen plume illustrates a consequence of the biotransformation process. The low dissolved oxygen zone is expected to closely approximate the distribution of the more mobile solutes (eg. benzene). This is because the low dissolved oxygen water will not be retarded, and any diffusion of dissolved oxygen into the plume will tend to be eliminated during the biotransformation of the mobile organic solutes (Borden et al., 1984). The more retarded species (eg. xylenes) should be swept by high dissolved oxygen water overtaking them, although this occurrence was not demonstrated during the field study.

Data from approximately 406 days after BTX injection indicates that the benzene mass loss curve has also tailed (Figure 4.5). From the results of two-dimensional model simulations, Borden et al. (1984) predict that the rate of mass loss with distance should decline (tailing) for unretarded hydrocarbons because of

Figure 4.11: The distribution of dissolved benzene and p-xylene at 26 days, and dissolved oxygen at 32 days after injection.



the lateral development of anoxic zones on either side of the plume front. This effect may explain the benzene tailing as well, although it requires further field evaluation. An alternative cause of the tailing, among other possibilities previously discussed in section 4.3.2, may be related to the preferential transport of the solutes along the low dissolved oxygen layer. Further sampling of the plume in Phase III will be conducted to assess the benzene persistence. It is hoped to use a "purge-and-trap" analytical procedure with a detection limit of 0.1 to 0.5 ppb benzene. This will help evaluate the possibility that biotransformation of benzene occurs only until a low-concentration level is attained.

4.6 Retardation

A plot showing the relationship between the solute travel distance and time, prepared from the centre of mass estimates, is presented in Figure 4.11. Data for benzene from 265 days and 410 days is not considered because the centre of benzene mass was not reliably determined on either occasion. Relative to chloride, the organic solutes are all retarded with the order of retardation from least to greatest as:

Benzene < toluene < o-xylene < p-xylene < m-xylene

This sequence is the same as that given by their order of increasing hydrophobicity, as expressed by their water solubilities and octanol-water partition coefficients (Table 1.1).

Roberts et al. (1985), in a previous study at the site, identified a trend towards increasing retardation with distance for several halogenated organic solutes. They suggested that this was caused by a deviation from local sorption equilibrium. Because the BTX solutes are relatively mobile, it is estimated that much larger travel times and distances are required before such a trend would be observed for these solutes. The apparent curving in Figure 4.12 and the possible decrease in benzene velocity through 265 and 410 days indicated in Figure 4.3 is likely a consequence of some other factors such as changing groundwater gradients or heterogeneities in aquifer properties.

The mobilities of the solutes can be compared by determining retardation factors for the organic solutes. The retardation factor, R, is defined as the ratio of the velocity of a non-reactive tracer, such as chloride, to the velocity of a reactive solute. With certain coarse assumptions it can be directly included in the advection-dispersion equation to account for sorptive solute behaviour (Bear, 1979; Freeze and Cherry, 1979).

Retardation factors calculated between neighboring pairs of sampling snapshots are presented in Table 4.4. It is apparent that the short-term retardation factors are quite variable. Between days 53 and 81, and days 81 and 108 the average retardation factor for the organic solutes fell from approximately 1 to less than 1, indicating that the mean travel velocities were at first slower and then faster than that of chloride. The chloride plume, in relation to the retarded organic plumes, was likely transported through zones of higher and lower conductivity, producing variable velocities. This behaviour is expected because the horizontal scale of the structural heterogeneities within the Borden aquifer (approxi-

Figure 4.12: Horizontal distances travelled by the centres of mass of the solutes.

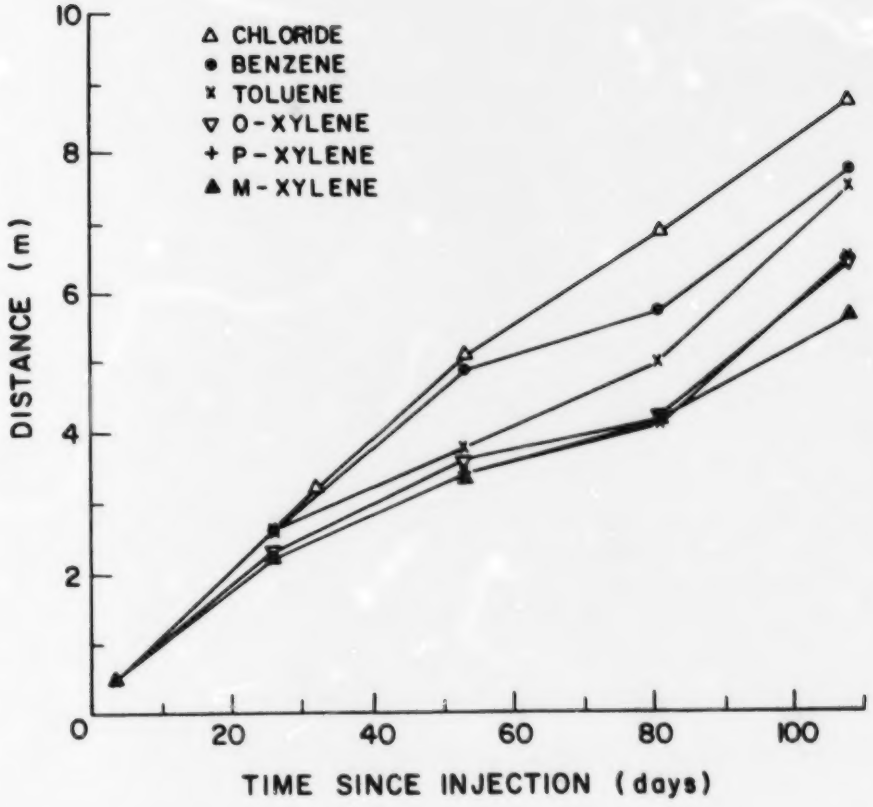


Table 4.4: Comparison of Retardation Factors

Solute	Day 3 -Day 26	Day 26 -Day 53	Day 53 -Day 81	Day 81 -Day 108	Average Day 3 -Day 108	Small Scale Tests*	Regression Equation**
Benzene	1.0	1.0	2.3	0.9	1.1	1.0-1.4	1.1
Toluene	1.0	2.0	1.4	0.7	1.2	1.2-1.5	1.2
o-Xylene	1.2	1.9	2.6	0.8	1.4	1.3-1.7	1.4
p-Xylene	1.3	2.0	2.5	0.8	1.4	1.4-2.0	1.5
m-Xylene	1.2	2.1	1.8	1.2	1.6	1.4-2.0	1.6

* described in detail by Patrick et.al. (1985)
** See text

mately 1.5 m; Sudicky, 1985) is comparable to the size of the plumes. Larger plumes should therefore tend to smooth this effect, while larger travel distances should tend to give more consistent values for the mean solute behaviour.

The effects of biotransformation on retardation are not apparent. No obvious relationships were found between the velocities of the solutes and the rates of mass loss. Perhaps biotransformations caused in part, some of the variance in the retardation factors, particularly at later times when the relative plume sizes became small.

To estimate mean solute behaviour, retardation factors were calculated between the first and last sampling snapshot. These are presented in Table 4.4 together with the predicted values derived from small scale batch and column tests (Ptacek et al., in press), and from a regression equation (Scharzenbach and Westall, 1981) which correlates the octanol-water partition coefficients of the organic solutes with the organic carbon content of the aquifer material.

The agreement in Table 4.4 between the field retardation factors and those predicted from the small scale tests, and particularly those from the regression equation are remarkable. The close agreement suggests that, for sandy aquifers with very low organic carbon contents such as the Borden aquifer, correlation equations may be very useful for predicting the retardation of certain organic solutes. The usefulness of such correlation equations, laboratory and small-scale field measurements for BTX in sand of higher organic carbon content is being evaluated further in Phase III and will be the subject of a subsequent report.

Chapter V

CONCLUSIONS

The results of the field study presented herein provide insight into the fate, persistence, and attenuation of dissolved petroleum hydrocarbons in shallow groundwater environments. It has been demonstrated that both mass losses and retardation of BTX solutes can occur in a shallow sand aquifer. The mass losses, which were 98 percent or greater for all organic solutes, are attributed to aerobic biotransformation processes, while retardation is attributed to sorption phenomena. At the Borden site these processes have combined to confer greater persistence to benzene over the other mono-aromatic solutes. The order among the solutes of the biotransformation rates is somewhat predictable, with benzene being the least transformable, followed by o-xylene, toluene and then m- and p-xylene. The order of retardation is also predictable, with benzene least retarded, followed by toluene, o-xylene, p-xylene and then m-xylene.

Retardation of these organics in the Borden sand is not sufficient to adequately evaluate the performance of the various calculation and small-scale tests used to predict the sorptive retardation. This evaluation must await the results of Phase III tests using sand with higher sorptive retardation capabilities. However, the possible irreversible sorption explanation for mass loss in the initial Phase I laboratory experiments does not seem warranted. Mass loss was most likely due to biodegradation.

Because of the low organic content and low clay content in the sand aquifer, retardation is not a prominent attenuation mechanism. The BTX solutes are all comparatively mobile, with average relative velocities to that of the groundwater ranging from 90% for benzene to 65% for m-xylene. Individual hydrocarbon velocities are variable, however, when measured over time intervals of about thirty days or less. This is likely a response of the small hydrocarbon plumes to changing groundwater gradients and local aquifer heterogeneities.

The dominant attenuation of BTX results from biodegradation. The mass losses of the BTX in the aquifer are characterized by a linear decline in total mass through time followed by a distinct tailing or rate reduction as small mass values are reached. In laboratory experiments linear decline in mass occurred at similar rates to those in the field, and tailing was also occasionally observed. Together, these studies suggest that the transformation process can be approximated by a zero order rate model, where oxygen is available. By doing so, however, the actual reaction kinetics may be oversimplified. When oxygen is limited and must be transported into the contaminant plume, biodegradation is slower, producing the observed tailing of mass loss rates. The sporatic persistence of benzene for more than 400 days is a consequence of an extremely slow biotransformation rate when oxygen is absent and the incomplete mixing of oxygenated water with the plume. Total mass loss, among other things, is a function of the plume size and shape, and will be affected by heterogeneous aquifer properties and conditions. Factors that

can control the mass loss process, such as the dissolved oxygen concentration, may produce a heterogeneous distribution of solute when they, themselves, are distributed heterogeneously.

An accurate interpretation of the results of an organic solute transport study may often require that the scale and magnitude of particular heterogeneities be known and accounted for in relation to known transport and attenuation processes. Studies such as that described herein, while requiring considerable effort for their design and implementation, will provide the necessary means and results to fully characterize natural transport processes under true field conditions. It is hoped that the results of this experiment and those underway in Phase III will indicate that less detailed studies will be sufficient to adequately define the critical field conditions at sites of contamination.

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Appendix A

ANAEROBIC MICROCOSM EXPERIMENTAL PROCEDURES

A.1 Introduction

Batch experiments were conducted to assess the fate of BTX under anerobic conditions and the effect of various nutrient additions on BTX biotransformation rates. The experiments were conducted in sealed hypovials, containing Borden material and groundwater spiked with BTX. These hypovial systems are commonly termed microcosms and attempt to establish conditions similar to those at the Borden field experiment. The analysis of BTX in microcosm solutions was performed by High Performance Liquid Chromatography (HPLC) so that only small aliquots of the microcosm solution would be required. This required the establishment of only a few microcosms because, rather than sacrificing a microcosm at each sampling time, the microcosm continues with only a subsample removed.

A.2 Microcosm Set-Up

Core material from the Canada Forces Base Borden field study, obtained from a depth of 1.5 - 3 meters, was mixed under a nitrogen atmosphere in a glovebox. The nitrogen was passed through a Supelpure (R)- oxygen trap to remove traces of oxygen. Mixing the sand ensures that microbial populations are evenly distributed. Twenty-five gram sand samples were added to sterile 60 ml hypovials (46 mL aqueous phase). Groundwater obtained from the same site was autoclaved and immediately purged with oxygen-free nitrogen gas overnight to minimize the oxygen concentrations. This reduced groundwater was added to each hypovial by repipet via teflon and stainless steel connections in the glovebox. Teflon mininert valves were installed without headspace. The flasks were removed from the glovebox and placed in a gas chamber set at 10°C. The chamber was evacuated and filled three times with oxygen-free nitrogen gas. Flasks taken randomly after set-up were examined for oxygen levels by a modified Winkler titration method and showed no detectable oxygen (less than 0.2 mg/L). The microcosms were incubated for one month before exposure to BTX to allow microbial populations to equilibrate.

BTX were added to each hypovial microcosm by microsyringe as neat solutions (no carrier solvent) to give initial concentrations of 3 mg/L of each organic. Various other additions were made to evaluate aerobic and anaerobic biotransformation in the presence of either nitrate, acetate, formate, lactate or no nutrient addition. In selected microcosms, aerobic conditions were established by injecting 250 ul of pure oxygen by gas tight syringe to give an oxygen concentration of 10

mg/L. Acetate, formate or lactate were added independently to selected microcosms as organic carbon sources to stimulate heterotrophic activity. Saturated aqueous solutions of each were added by microsyringe to give a concentration of 100 mg/L each. An aqueous solution saturated with sodium nitrate was added to selected microcosms as an alternate electron acceptor to oxygen, by microsyringe to give an initial nitrate concentration of 100 mg/L. Microcosms and controls were established in triplicate or duplicate. Only the anaerobic experiments with no nutrient additions are described in this report. The other experiments will be described in subsequent reports.

A.3 HPLC Analysis

Analysis of BTX was by HPLC using a Spherisorb S5 ODS II (C18) reverse phase column (25 cm) with a isocratic mobile phase of 70% acetonitrile and 30% water at 1 mL/min, to separate and elute the BTX sequentially prior to detection. A Supelco C18 guard column was installed ahead of the analytical column to trap particles and retain highly-sorbed organics. The HPLC grade acetonitrile (Baker analyzed) was passed through 10 cm x 2 cm of alumina oxide (acidic) and the deionized distilled water was passed through a MilliQ water purification system and then passed through 10 cm x 2 cm of Chromosorb 101 to remove impurities. A 100 uL sample from the microcosm was injected into a Rheodyne 7161 injector with a mobile water phase. A 25 cm column packed with Chromosorb 101 was installed between the water reservoir and pump to purify this water as well. BTX were concentrated inline on a uptight short column (3 cm x 4 mm) packed with S5 ODS II. After concentration (30 seconds) the acetonitrile/water mobile phase was backflushed through the short column by means of a Rheodyne 7000 switching valve onto the analytical column. P- and m-xylene coelute and so either m-xylene alone was employed or, where both were employed, the results are reported as p- plus m-xylene. Separation took 10 minutes. Detection was by a Gilson monochrom UV detector at 210 nm absorbance with a minimum detection limit of 50 ug/L for benzene and 30 ug/L for toluene and xylenes. Quantification and identification was by comparison to pure external standards. Stock solutions and standards were prepared as previously reported (Patrick et al., 1985, Appendix D). Before analysis standards were run to insure that quantification was within 10% of predicted value.

The accuracy, precision and method detection limits (MDL) for the HPLC analysis is presented in Table A.1. Due to coelution, the p- and m-xylene results are reported as the sum of each isomer. The average relative error is less than 10% and the relative standard deviation is less than 15% at the BTX concentrations shown. Near the MDL this accuracy and precision is expected to be poorer.

Table A.1: Accuracy and Precision of the HPLC Analysis for BTX at Typical Sample Concentrations and the Estimated Method Detection Limit

Compound	*N*	*S%*	*X (± SE)*	X_o	*E%*	*MDL*
benzene	6	8	141.0+11.0	141.6	-0.4	50
toluene	6	13	151.6+20.0	141.0	+8	30
o-xylene	6	10	128.2.+12.5	138.1	-7	30
p-plus m-xylene	6	8	186.7+21.7	280.8	+2	30

all results in ug/L
N: number of replicate determinations
S%: relative standard deviation
X(+SE): mean of replicate determinations (± standard error)
X_o: true value
E%: average relative error
MDL: estimated method detection limit